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ANALYSIS AND CHARACTERIZATION OF ORGANIC CARBON COMPOUNDS IN ATMOSPHERIC PARTICULATE MATTER

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Estimation of the soot or light absorbing carbon collected on Teflon and quartz filters by use of light absorption methods (light transmission and photoacoustic) compared favorably with the combustion procedure used to measure soot carbon.

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I. SELECTIVE SOLVENT EXTRACTION AND LIQUID CHROMATOGRAPHY

INTRODUCTION

The extraction of a solute from one liquid phase into another liquid phase is one of the most simple and rapid separation techniques in analytical chemistry. When two immiscible solvents, typically an aqueous and organic phase, are placed in contact with each other, a substance which is soluble in both of them distributes, or partitions, itself between the two phases. Solvent extraction has been widely used for separation of both inorganic and inorganic species. The nature of the organic solvent has a considerable effect on the course of the extraction, particularly in organic analyte systems.

The Hildebrand solubility parameter which is defined as the square root of the cohesive energy density in a liquid, is a quantitative measure of the dispersion interactions occurring between two liquids. Since non-polar compounds have relatively weak dispersion interactions, while polar compounds will have relatively strong interactions, the solubility parameter is generally referred to as a measure of the polarity of organic compounds. Values of δ range from 7.0 for isooctane (non-polar) to 21.0 for water (polar). In liquid-liquid partition chromatography, the solubility parameter can be related to the distribution constant K by the following formula:

$$\ln K_i = \frac{V_i \left[(\delta i - \delta m)^2 - (\delta i - \delta s)^2\right]}{} \qquad \text{(I-1)}$$

where δ_i, δ_m, and δ_s = the solubility parameters of solute i, mobile phase m, and stationary phase s, respectively,

$\overline{V}_i$ = molar volume of solute i

R = gas constant (1.987 ca./°K/mole

T = absolute temperature

K_i = distribution constant for solute i

Since the distribution constant K can be related to the retention volume by:

$$V_R = V_m + KV_s \qquad \text{(I-2)}$$

where

V_R = retention volume

V_m = mobile phase or void volume

V_s = stationary phase volume

equation (1) can be used to relate the solubility parameter with retention volume. Ideally, by knowing the solubility parameters of the two phases and the solute, one could prodict the retention volume of the solute. By extension, the identification of experimental conditions necessary for the successful separation of mixtures would also become much more simplified, allowing the chromatographer to develop complex separations easily and routinely.

Solubility parameter theory, as originally developed by Hildebrand, assumed that only dispersion forces were important in describing the intermolecular interactions in a liquid. Several refinements of this basic approach have been proposed, although the most useful approach appears to be the so-called "three-dimensional" solubility parameter system. The basis of the three-dimensional system is the assumption that the total cohesive energy of the liquid E, can be divided into contributions from dispersion forces, E_d, permanent dipole-permanent dipole forces, E_p, and hydrogen-bonding forces, E_h. Thus,

$$E = E_d + E_p + E_h \qquad \text{(I-3)}$$

Dividing this equation by the molar volume of a solvent, V, gives

$$\frac{E}{V} = \frac{E_d}{V} + \frac{E_p}{V} + \frac{E_h}{V} \qquad \text{(I-4)}$$

or

$$\delta^2 = \delta_d^{\,2} + \delta_p^{\,2} + \delta_h^{\,2} \qquad \text{(I-5)}$$

where

$$\delta = (E/V)^{1/2} \qquad \text{(I-6)}$$

the usual equation for the Hildebrand solubility parameter.

Each component of the overall solubility parameter measures a different kind of molecular interaction. Although the overall solubility parameter for a variety of solvent mixtures may remain constant, the values for δ_d, δ_p, δ_h may vary widely. Changes in the values of δ_d, δ_p, δ_h could therefore have a drastic effect upon the distribution behavior of a solute.

Liquid-liquid partition chromatography is based on the equilibrium distribution of an analyte between a mobile phase and a stationary phase. In a fundamental sense, liquid chromatography is a multi-stage extraction, and, as such, many of the principles of solvent extraction should be applicable to chromatography.

Porous polystyrene-divinylbenzene resins have been widely used for a number of years as supports in both liquid-liquid (LLC) and liquid-solid (LSC) chromatography. Most of the resins used have had relatively large particle diameters typically in the range of 50-200 mesh, or 300-75 um, and have been suited more for gravity-flow column chromatography than high pressure liquid chromatography. In recent years, manufacturers, particularly in Europe and Japan, have made porous polymer packings especially designed for use in high pressure liquid chromatography.

Macroporous polymers have two major advantages over silica-based materials which make them exciting stationary phases in liquid chromatography. They are suitable for use in both normal phase and reverse phase modes, depending upon the particular mobile phase used. Polymer based materials are also stable over the entire pH range, allowing the chromatographer to employ a much wider spectrum of mobile phases than can be used with silica materials. Polymer materials have the disadvantage that they tend to swell

and shrink slightly with different mobile phases but for most applications, this is not a problem.

The relative distribution of a sample component of i between two phases is determined by the intermolecular interactions of a molecule of i with the molecules of the mobile and stationary phases. The phase that interacts more strongly with component i will contain a proportionately higher concentration of i. In a fundamental sense, the relative strengths of these solute-solvent interactions are determined by the kinds and magnitude of the different intermolecular forces. The polarities of both the sample and solvent as defined by the Hildebrand approach discussed earlier can be used as a general guide to the strengths of these interactions.

EXPERIMENTAL

Chromatograms for this study were obtained using one of two chromatographs. One chromatograph consisted of a Spectra-Physics 3500B Gradient Liquid Chromatograph equipped with a Valco injector valve and a Spectra-Physics SP8200 UV/Visible Detector operated at 254nm. The second chromatograph was assembled using an Altex Model 110A pump, a Valco injector valve, and a Schoeffel SF 770 Spectroflow detector also operated at 254 nm. For both chromatographs, a Houston Instrument Omniscribe A-5211 recorder was used to record the chromatograms, and a Spectra-Physics System 1 Integrator was used to determine peak retention times.

A pre-packed Shawa-Denko Polymerpak SP500 column and a second column packed in the laboratory were used in this study. The SP500 column is packed with porous styrene-divinylbenzene polymer beads, nominally 15-20u in diameter. The second column was packed with the bulk beads, designated D-814, using a Micromeritics Model 705A slurry packing apparatus. The mobile phase used to pack the column was 50:50 methanol: water.

Chloroform, methanol, ethanol, acetonitrile, water, and 2,2.4-trimethylpentane (isooctane), along with various mixtures of these solvents, were used as mobile phases. Methanol was AR grade (J. T. Baker), isooctane and acetonitrile were spectrophotometric grade (Scientific Products) ethanol was absolute (U. S. Industries), and all were used as received. Distilled, deionized water was used throughout. Chloroform (AR grade, Mallinckrodt) was washed three times with equal volumes of water, dried over calcium chloride, and distilled. Prior to use, organic mobile phases were filtered through a 0.5μ pore size Schleicher and Schuell TE 36 Teflon filter, while water was filtered using a 0.45μ pore size Schleicher and Schuell OE 67

cellulose acetate filter. All mobile phases were degassed by stirring for a few minutes under reduced pressure.

The following AR grade chemicals, except as noted, were used as solutes: benzene, chlorobenzene, nitrobenzene, toluene, ethylbenzene, m-xylene, and p-xylene (J. T. Baker); dibutylphthalate 99%, dioctylphthalate, dimethylphthalate 99%, n-butylbenzene 99+%, cumene 99%, cumene 99% (isopropylbenzene), n-propylbenzene 98%, 2-chloroaniline 98+%, 4-chloroaniline 98%, aniline 99.9+%, o-nitroaniline 98%, and anthranilic acid 98+% (o-aminobenzoic acid), (Aldrich); benzoic acid primary standard, cinnamic acid, phthalic acid, and salicylic acid (Mallinckrodt); phenol, catechol, resorcinol, and hydroquinone (Eastman grade); and naphthalene, phenanthrene and pyrene (Eastman technical grade). Napththalene, phenanthrene, and pyrene were each twice recrystallized from ethanol-water; the remaining solutes were used without further purification. These solutes were chosen as representative aromatic compounds with a variety of functional groups.

Solutions of from 1-1000 ppm were used. The solutes were dissolved in one of the components of the mobile phase to be used, and the particular solute concentrations were chosen to obtain the desired detector response. After the column was equilibrated with the desired mobile phase, a 10 µL sample of each of the solutes was injected, and its chromatogram and retention time were recorded.

CALCULATION OF CHROMATOGRAPHIC PARAMETERS

One of the most important quantities used to describe separation in a distribution system is the capacity factor k', defined as:

$$k' = \frac{\text{total amount of solute in phase x}}{\text{total amount of solute in phase y}} \qquad \text{(I-7)}$$

The total amount of solute in a particular phase can be expressed as (C)(V), where C represents the solute concentration and V represents the phase volume. Thus, equation (7) can be written:

$$k' = \frac{C^x V^x}{C^y V^y} \qquad \text{(I-8)}$$

Since the solute distribution constant K is defined as $\frac{C^x}{C^y}$, equation (8) may be written:

$$k' = \frac{V^x}{K(V^y)} \qquad \text{(I-9)}$$

(Phase x is defined to be the stationary phase in chromatography.)

In chromatographic systems, the primary retention parameter is the retention volume V_R, defined as $(t_R)(F)$, where t_R is the time required for the elution of a solute from the column, and F is the volumetric flow rate of the mobile phase. Another useful parameter is the mobile phase volume V_m, which is the total volume of mobile phase within the column. V_m can be determined from $V_m = (t_o)(F)$, where t_o is the time for elution of a non-retained solute.

A useful measure of retention is R, the fraction of solute in the mobile phase.

$$R = \frac{n_m}{n_m + n_s} \qquad \text{(I-10)}$$

where n_m and n_s are the total moles of solute in the mobile and stationary phases, respectively. Since $k' = (n_s/n_m)$,

$$R = \frac{1}{1 + k'} \qquad \text{(I-11)}$$

The average migration velocity V_s of a solute is equal to the mobile phase velocity, V, times the fraction R of solute in the mobile phase at any given time:

$$V_s = VR \qquad \text{(I-12)}$$

$V_s = L/t_R$, where L is the column length, and $V = L/t_o$. Since $t_R = V_R/F$, and $t_o = V_m/F$, substituting these expressions into the forms of V_s and V, and then substituting into equation (12) gives:

$$\frac{LF}{V_R} = \frac{(LF)(R)}{V_m} \qquad \text{or} \qquad \text{(I-13a)}$$

$$V_R = \frac{V_m}{R} \qquad \text{(I-13b)}$$

Substituting equations (11) into (13b) gives:

$$V_R = V_m (1 + k') \qquad \text{or} \qquad \text{(I-14a)}$$

$$V_R = V_m + KV_s \qquad \text{(I-14b)}$$

Equations (14a) and (14b) describe the fundamental relationship between migration and equilibrium of a solute within a column. It is a much simpler experimental task to measure V_R and V_M than it is to measure V_s. Experimentally, the k', rather than k, is determined from equation (14a):

$$k' = \frac{V_R - V_m}{V_m} \qquad \text{(I-15)}$$

In gas chromatography, it has been observed that a straight line relationship exists between the log retention volume and the carbon number in a homologous series (1, 2). This same effect has also been observed for several liquid chromatographic systems (3, 4). In an attempt to determine if the D814 packing would exhibit similar results, the chromatographic behavior of the solutes benzene, toluene, ethylbenzene, n-propylbenzene, n-butylbenzene, and cumene (isopropylbenzene) was investigated. Table 1 and Figures 1 and 2 show the results obtained for the six solutes when operating the column in the normal phase mode. (n-propylbenzene, n-butylbenzene and cumene exhibited essentially identical chromatographic behavior; therefore, only the results for n-propylbenzene were plotted).

Table 1

Log k' values for Benzene (B), Toluene (T), Ethylbenzene (E), n-propyl Benzene (n-PB), n-Butyl Benzene (n-BB), and Cumene (C) with Isooctane-Chloroform and Isooctane-Ethanol Mobile Phases

	log k'					
Mobile Phase	B	T	E	n-PB	n-BB	C
Iso:$CHCl_3$						
100:0	-0.28	0.08	-0.07	-0.22	-0.21	-0.47
85:15	-0.96	-0.88	-0.99	-0.89	-0.89	-0.92
75:25	-1.00	-1.10	-1.15	-0.82	-0.85	-0.89
50:50	-1.04	-1.15	-1.30	-2.00	-1.70	-2.00
25:75	-1.15	-1.40	-2.00	-1.70	-1.70	-2.00
0:100	-1.70	*	*	-1.50	-1.70	-1-50
Iso:EtOH						
100:0	-0.28	0.08	-0.07	-0.22	-0.21	-0.47
91:9	-0.29	-0.16	-0.30	-0.48	-0.48	-0.54
82:18	-0.23	-0.16	-0.29	-0.43	-0.42	-0.51
72:28	-0.32	-0.16	-0.26	-0.43	-0.43	-0.51
63:37	-0.26	-0.21	-0.30	-0.42	-0.41	-0.49
0:100	-0.25	0.04	0.08	0.049	0.11	0.017

*eluted with void volume

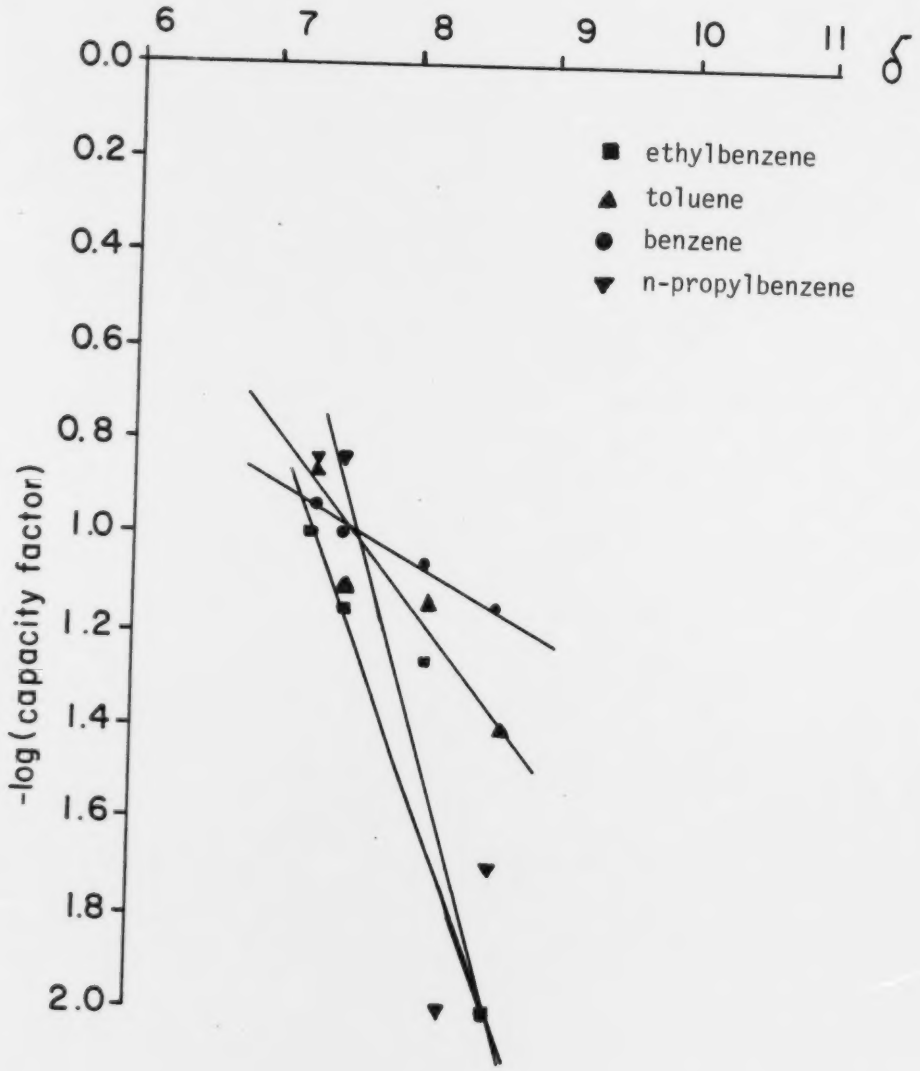


Figure 1. Log (Capacity Factor)-Solubility Parameter Relationship Using Isooctane-Chloroform

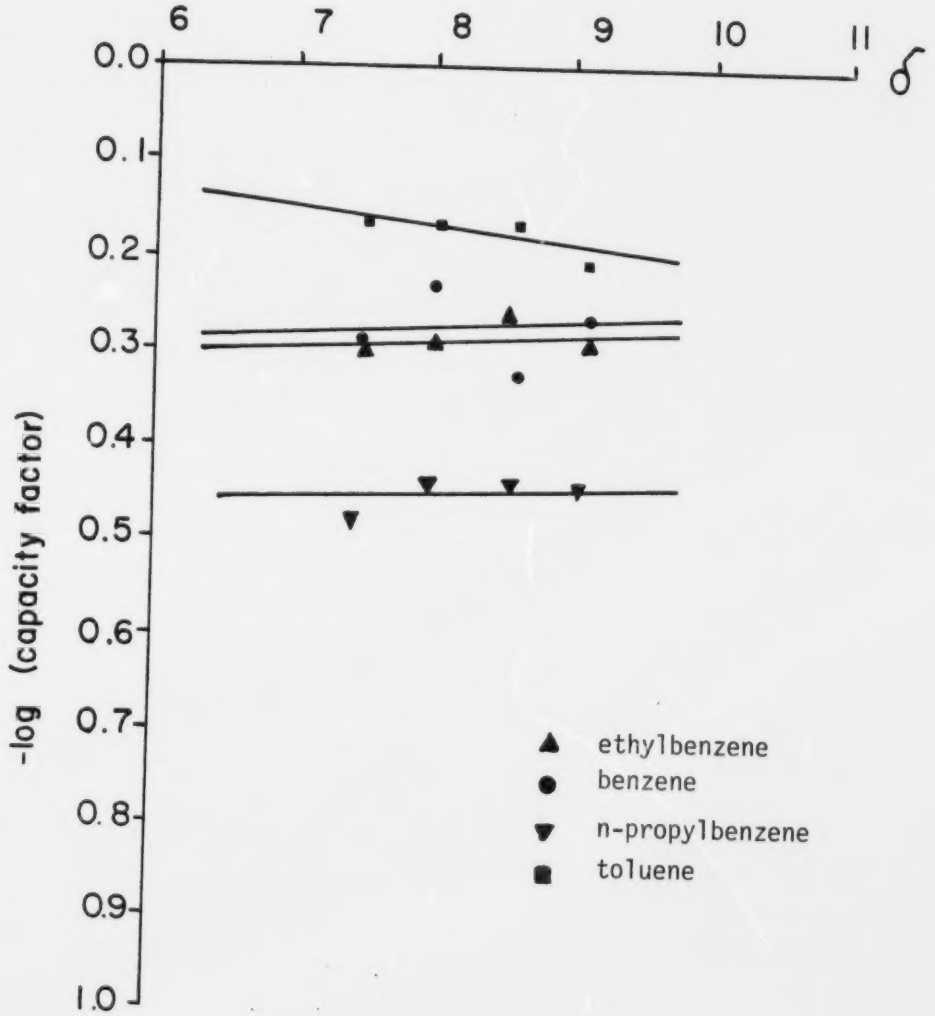


Figure 2. Log (Capacity Factor)-Solubility Parameter Relationship Using Isooctane-Ethanol

An examination of Figure 1 would indicate that a good separation of benzene, toluene, and ethylbenzene should be possible. However, since Figures 1 and 2 are plots of log k' rather than k', any differences in k' values for the various solutes tend to become exaggerated. In fact, the actual differences in k' for the solutes are very small, and within experimental error for this data. This is shown more clearly in Table 2, which lists the actual k' values for the solutes.

Table 2

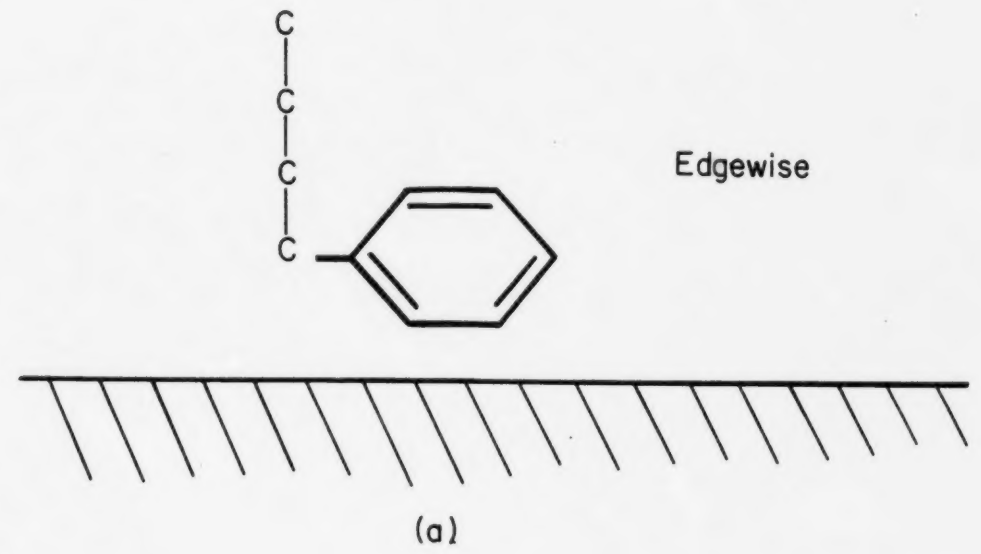
k' Values for Benzene (B), Toluene (T), Ethylbenzene (E), n-Propyl Benzene (n-PB), n-Butyl Benzene (n-BB) and Cumene (C) with Isooctane-Chloroform and Isooctane-Ethanol Mobile Phases

	k'					
Mobile Phase	B	T	E	n-PB	n-BB	C
Iso:$CHCl_3$						
100:0	0.52	1.21	0.85	0.60	0.62	0.34
85:15	0.11	0.13	0.10	0.13	0.13	0.11
75:25	0.10	0.08	0.07	0.15	0.14	0.13
50:50	0.09	0.07	0.05	0.01	0.02	0.01
25:75	0.07	0.04	0.01	0.02	0.02	0.01
0:100	0.02	0	0	0.03	0.02	0.03
Iso:EtOH						
100:0	0.52	1.21	0.85	0.60	0.62	0.34
91:9	0.51	0.69	0.50	0.33	0.33	0.29
82:18	0.58	0.69	0.52	0.37	0.38	0.31
72:28	0.47	0.69	0.55	0.37	0.37	0.31
63:37	0.54	0.61	0.51	0.38	0.39	0.32
0:100	0.56	1.09	1.20	1.12	1.29	1.0-

As noted previously, n-propylbenzene, n-butylbenzene, and cumene have essentially the same retention on the column. With a few exceptions, the retention of these three solutes is essentially identical, within experimental error, to that of benzene, toluene, and ethylbenzene. Each of the six solutes, therefore, intereacts with the column in the same manner, despite the fact that the size of the aliphatic side-chain is increasing.

Since the side-chain has no effect on the retention of the solutes, the interaction between the solutes and the column must occur through the benzene ring. This suggests two possible orientations for the solutes on the surface of the adsorbent, as illustrated in Figure 3. In Figure 3(a), the benzene ring is sitting on its edge, while in Figure 3(b), the benzene ring is lying flat on the surface. In each case, the aliphatic side-chain must extend away from the surface.

The addition of a methyl group to the benzene ring to form toluene should increase the area of the molecule from 51 $\mathring{A}^2$ to 57.5 $\mathring{A}^2$ (5). Since it has been shown that the retention of a solute on D814 beads depends upon size, the increase in the molecular area upon going to toluene would be expected to change the retention of the substituted aromatics. The configuration in Figure 3(a) would then be favored, since no change in retention was observed for any of the solutes. It is unlikely, however, that the aromatic compounds interact with the surface through hydrogen bonding, as would be the case in Figure 3(a). Despite the fact that the molecular area is increased slightly, the preferred configuration for the solutes is that of Figure 3(b). The observation that the aromatic group adsorbs in a flat configuration is consistent with what is observed when other stationary phases are used (6). This observation also supports the idea that the interaction between the solute and stationary phase occurs through the π-electron system.



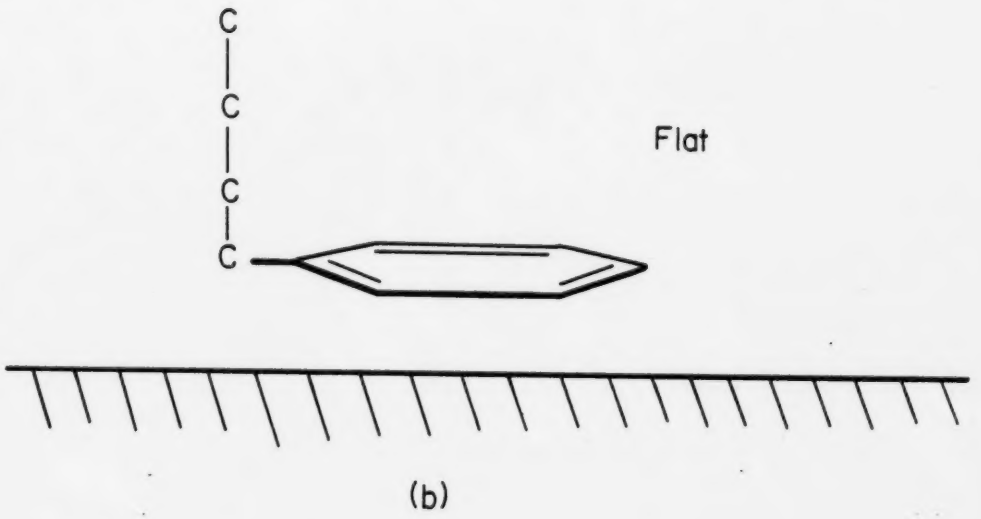


Figure 3. Possible Orientations for Solutes on Surface of the Adsorbent

Table 3

Log k' Values for Benzene (B), Toluene (T), Ethylbenzene (E), n-Propyl Benzene (n-PB), n-Butyl Benzene (n-BB) and Cumene (C) with Chloroform-Methanol and Chloroform-Acetonitrile Mobile Phases

	log k'					
Mobile Phase						
$CHCl_3$:MeOH						
100:0	-1.70	*	*	-1.50	-1.70	-1.50
90:10	-1.10	-1.00	-1.04	-1.70	-2.00	-1.70
75:25	-1.10	-0.93	-0.92	-1.20	-1.20	-1.20
50:50	-0.96	-0.70	-0.84	-0.80	-0.80	-0.80
25:75	-0.57	-0.55	-0.50	-0.49	-0.43	-0.58
0:100	-0.06	-.003	0.06	0.10	0.22	0.040
$CHCl_3$:CH_3CH						
100:0	-1.70	*	*	-1.50	-1.70	-1.50
82:18	-1.30	-1.30	-1.40	-1.20	-1.20	-1.20
52:48	-0.97	-0.89	-0.84	-0.74	-0.74	-0.74
0:100	-0.49	-0.42	-0.34	-0.31	-0.24	-0.35

*eluted with void volume

Table 3 and Figures 4 and 5 summarize the results obtained when the column was operated in the reverse phase mode. Once again, as the results show, all of the solutes exhibited behavior that was nearly identical to that of benzene.

The results obtained with the aliphatic substituted aromatics suggest that the D814 packing would be suitable for separating certain classes of compounds, but would not be suitable for separating individual compounds within classes. Figure 6, a plot of retention volume vs. mobile phase solubility parameter for benzene, naphthalene, phenanthrene, and pyrene, shows that mobile phases with solubility parameters of either approximately 8 or 12 should be suitable for separating these four compounds. A 50:50 $CHCl_3$:MeOH mobile phase (δ = 11.8) was chosen, and when a mixture of the four solutes was injected, baseline separation of the four solutes was obtained. On the other hand,

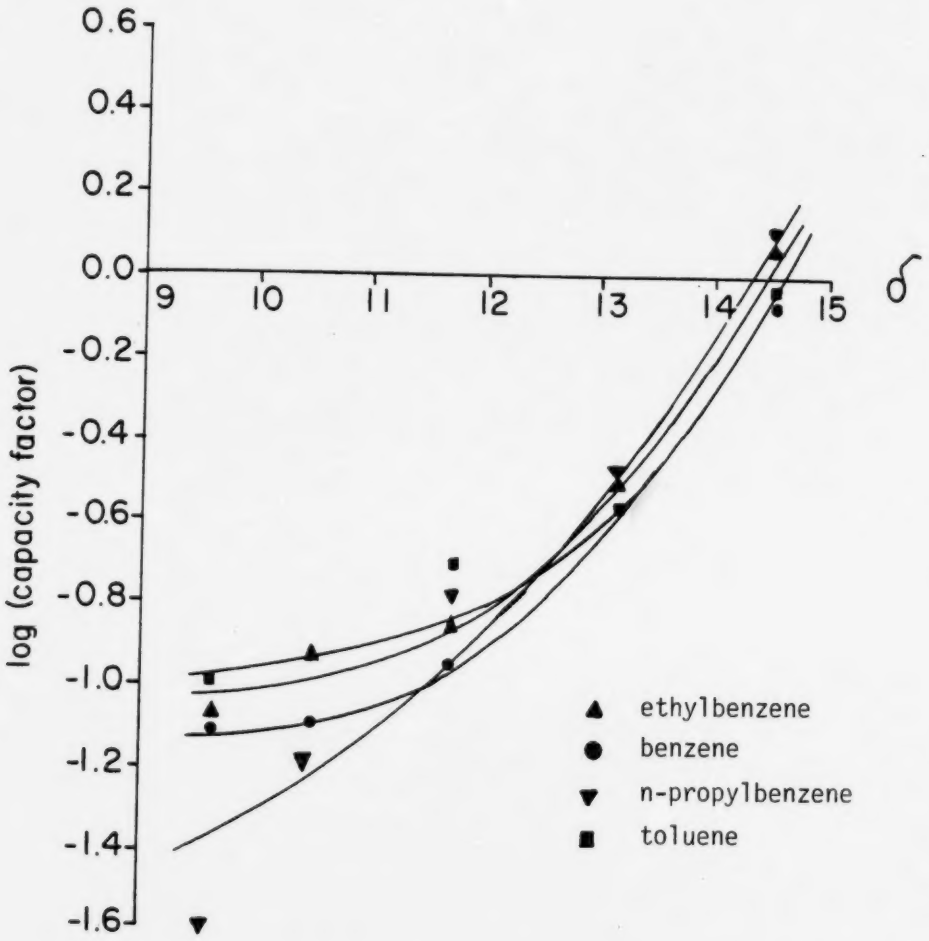


Figure 4. Log (Capacity Factor)-Solubility Parameter Relationship Using Chloroform-Methanol

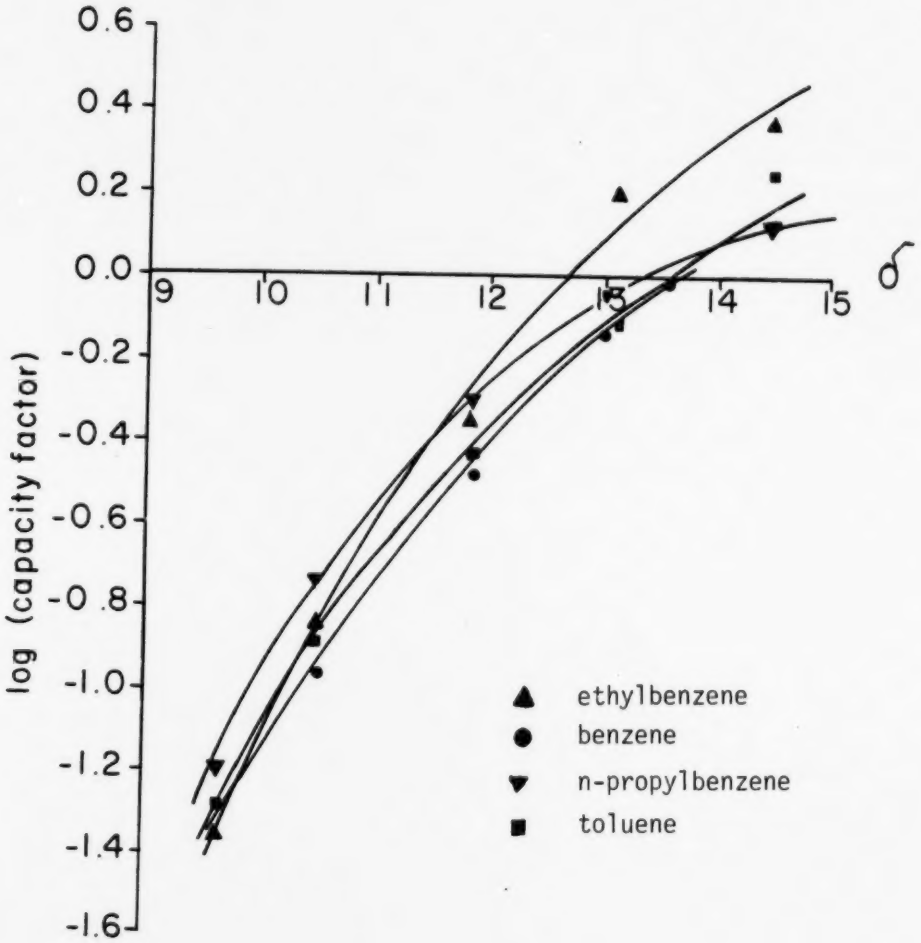


Figure 5. Log (Capacity Factor)-Solubility Parameter Relationship Using Chloroform-Acetonitrile

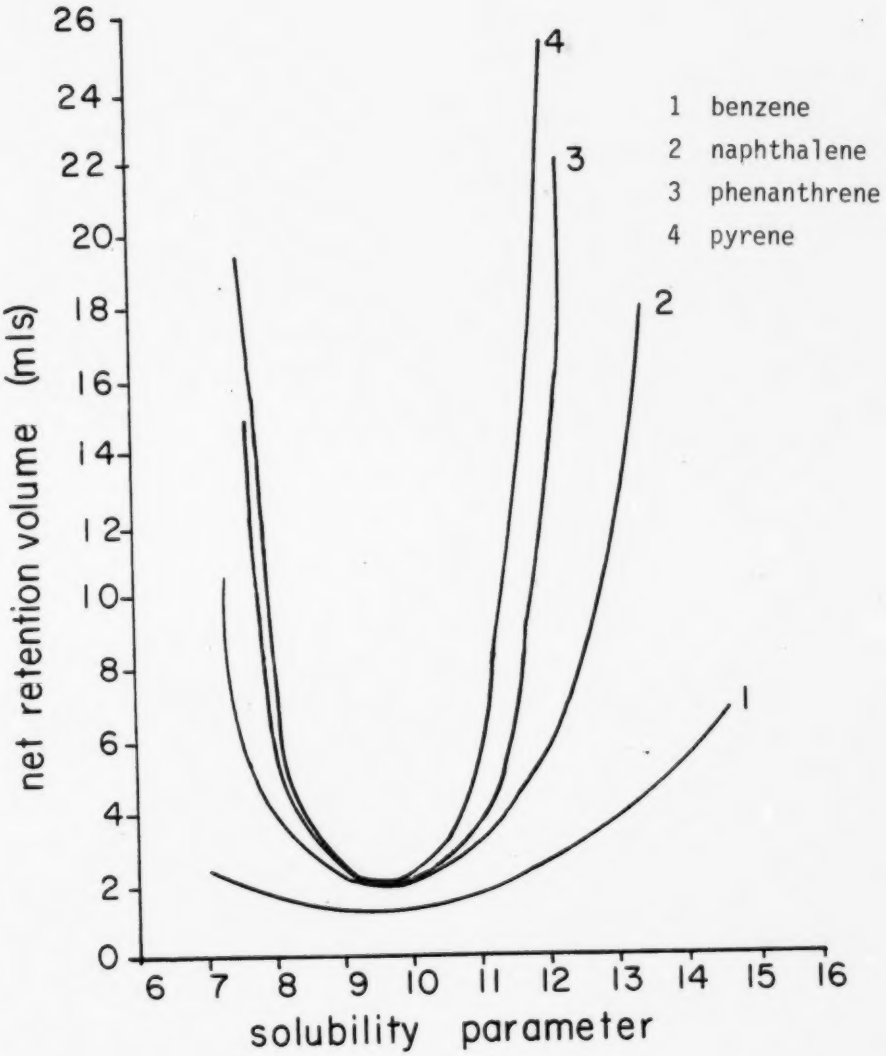


Figure 6. Retention Volume-Solubility Parameter Relationship

a mixture of benzene, toluene, ethylbenzene, and n-propylbenzene did not separate, but instead gave one broad peak.

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II. CHROMATOGRAPHIC BEHAVIOR OF POLYCYCLIC AROMATIC HYDROCARBONS

The chromatographic behavior of four polycyclic aromatic hydrocarbons (PAHs) of environmental interest, benzene, naphthalene, phenanthrene, and pyrene, was investigated using both the normal phase and reverse phase modes. Table 4 below lists the solubility parameters for the four solutes. Tables 5 and 6 list the mobile phases used in the normal phase mode.

Table 4

Solute	Solubility Parameter (1)
Benzene	9.2
Naphthalene	9.9
Phenanthrene	9.8
Pyrene	10.5

Table 5

Isooctane - Chloroform Mobile Phases

Iso:$CHCl_3$ Radio	Solubility Parameter
100:0	7.0
85:15	7.3
75:25	7.5
50:50	8.1
25:75	8.6
0:100	9.2

Table 6

Isooctane: Ethanol Mobile Phases

Iso:EtOH Ratio	Solubility Parameter
91:9	7.5
82:18	8.1
72:28	8.6
63:37	9.2
0:100	12.7

Figure 7 is a plot of log k' for each solute vs. mobile phase solubility parameter for the isooctane:chloroform mobile phases. Each solute exhibits a linear relationship between log k' and solubility parameter. A comparison between Figure 1 and Table 4 shows that the elution order of the solutes is not the same as would be predicted based upon their solubility parameters, viz., phenanthrene would be predicted to elute before naphthalene. This indicates that some mechanism other than strictly solubility parameter is at play in determining the distribution, and hence the elution, of these solutes.

In size exclusion chromatography (SEC) using polystyrene packings, the packing material is often considered to be a gel. SEC packings have a low percentage cross-linking (2), which results in a gel-like material. Shodex D814 packing has a much higher percentage cross-linking (3), and hence should probably be considered as a solid rather than as a gel or liquid.

Karger (4) indicates that in LSC the adsorbent surface is covered by a monolayer of mobile phase molecules. In order for a solute molecule to be adsorbed onto the stationary phase, it must first displace a certain number of mobile phase molecules. In a sense, then, the solute and solvent molecules are in competition for the stationary phase. The forces involved in the competition can be divided into 2 broad categories: (1) dispersive or non-specific forces, and (2) specific forces, such as induction,

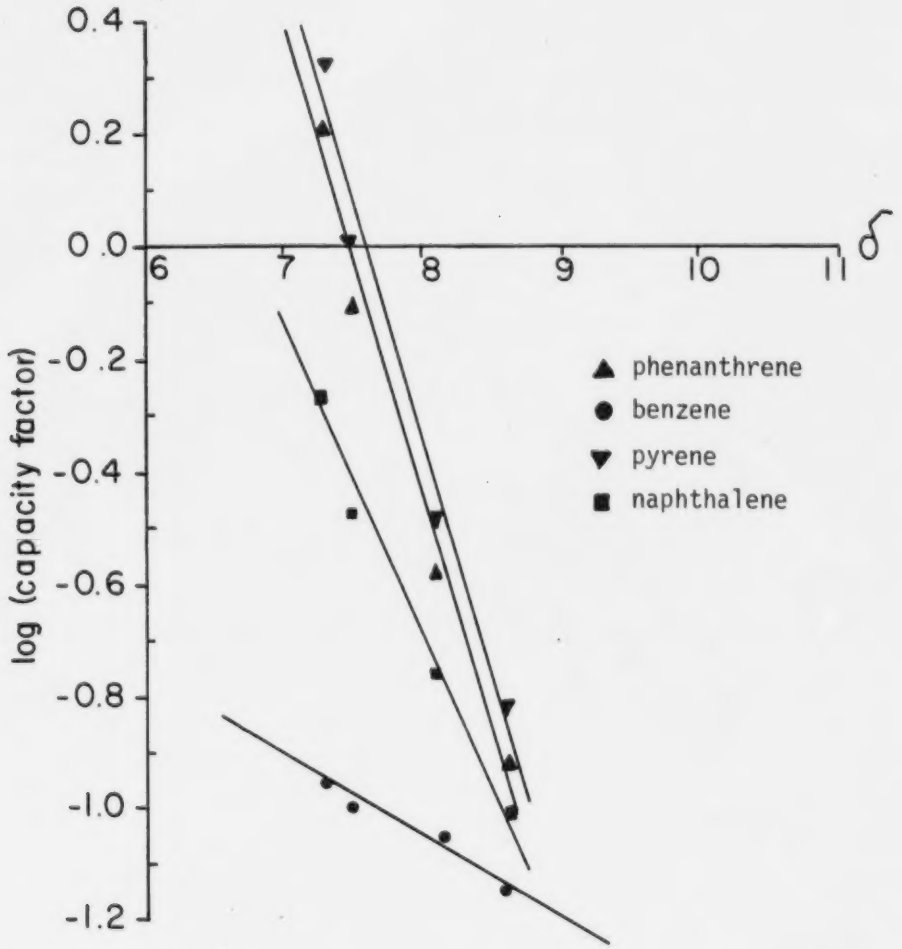

Figure 7. Log (Capacity Factor)-Solubility Parameter Relationship Using Isooctane-Chloroform

electrostatic interactions, and hydrogen bonding (5).

Karger's description of LSC assumes that the support upon which the monolayer of stationary phase is adsorbed is a solid, uniform sphere. It is likely, however, that in the case of porous polystyrene beads the situation is somewhat different. Pietzryk (6) has shown that XAD resin and a polystyrene resin with 8% divinylbenzene cross-linking (p-80) have large and selective uptakes of organic solvents. For the P-8D resin, for example, he found an uptake of 0.050 grams of methanol per gram of resin, while the uptake of chloroform was 1.40 grams per gram of resin. The table below summarizes Pietrzyk's results

Table 7

Uptake of Solvents by P-8D Resin (from Pietrzyk(6))

Solvent	Uptake (gm solvent/gm resin)	Solubility Parameter
Water	0.054	21
Methanol	0.050	14.5
Ethanol	0.062	12.7
Acetonitrile	0.171	11.9
Chloroform	1.40	9.1
Benzene	0.724	9.2
Hexane	0.015	7.3
Cyclohexane	0.005	8.2
P-8D Resin		9.1

As indicated above, the resin uptakes to a greater extent solvents that are chemically similar to it as measured by the solubility parameter. Although he did not measure the uptake of solvent mixtures, it is likely that one component of a mixture would be selectively adsorbed by the resin. Indeed, Schill (7) has shown this to be the case for acetonitrile-water mixtures on C-18 coated silica.

Figure 8 is also a plot of log k' for benzene and naphthalene vs. mobile phase solubility parameter for the isooctane:ethanol mobile phases (phenanthrene and pyrene did not elute with these mobile phases). For both solutes there is a linear relationship between log k' and solubility parameter; however, as Figure 8 and Table 8 show, the value for log k' remains essentially constant for each mobile phase.

Table 8

log k' for Benzene and Naphthalene as a Function of Isooctane:Ethanol Ratio

Isooctane:Ethanol	log k'	
Ratio	Benzene	Naphthalene
100:0	-0.28	0.70
91:9	-0.29	0.40
82:18	-0.23	0.40
72:28	-0.32	0.40
63:37	-0.26	0.39
0:100	-0.25	0.59

The k' values for each of the four solutes using isooctane-ethanol mobile phases are larger than the corresponding values for the isooctane-chloroform mobile phases. This indicates that the solutes have a lower affinity for the stationary phase when chloroform is in the mobile phase. In other words, the stationary phase preferentially adsorbs chloroform, forming a layer which prevents the solutes from interacting with the surface of the beads. This is consistent with the results obtained when measuring the bulk distribution constants.

The elution order of the solutes is a function of their molecular areas (A_s). A_s values for unsubstituted hydrocarbons of the formula C_cH_h can be calculated using the formula (8):

$$A_s = 6 + 0.8\ (h-6) + 0.25\ (c-h) \qquad \text{(II-1)}$$

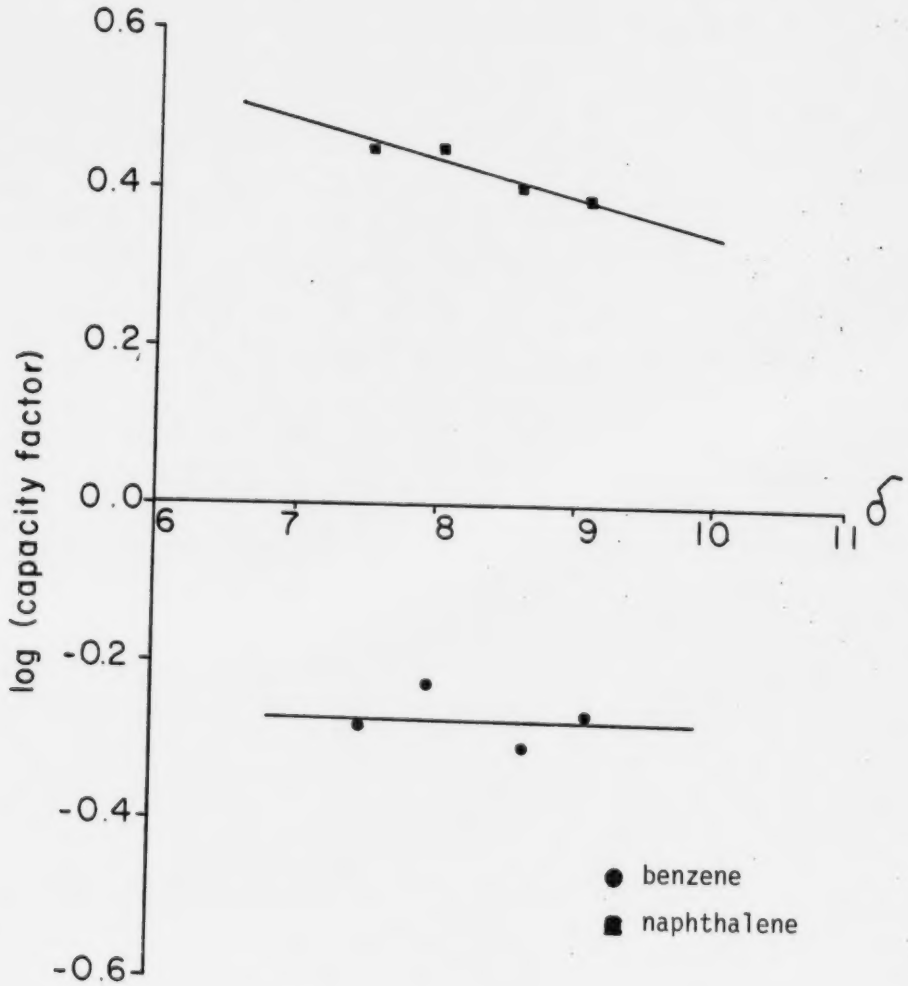

Figure 8. Log (Capacity Factor)-Solubility Parameter Relationship Using Isooctane-Ethanol

A_s is an arbitrary scale to conveniently measure the relative areas of molecules, and is related to their actual areas by the factor 8.5 $\mathring{A}^2$ per unit of A_s (9).

The relative retention volumes for the four solutes were benzene < naphthalene < phenanthrene < pyrene. Table 9 below lists the molecular areas for the four solutes.

Table 9

Solute	A_s	$\mathring{A}^2$
Benzene (C_6H_6)	6	51
Naphthalene ($C_{10}H_8$)	8.1	69
Phenanthrene ($C_{14}H_{10}$)	10.2	87
Pyrene ($C_{16}H_{10}$)	10.7	91

As may be seen, the retention volume increases as the molecular size increases. Based on the size of the molecules, the chromatographic behavior of benzene, naphthalene, and phenanthrene would be predicted to differ significantly, while the behavior of phenanthrene and pyrene would be predicted to be very similar. Figures 7 and 8 show this to be the case. In all of the mobile phases used, phenanthrene and pyrene exhibited essentially the same behavior, which in turn differed from that of benzene and naphthalene. Since the elution order correlates with size, the forces involved in the interaction between the stationary phase and the solutes are non-specific forces. These non-specific forces are likely to be π-electron system interactions between the solutes and the styrene-divinylbenzene matrix (10).

Tables 7 and 8 illustrate this point more dramatically.

Table 10

Overall Solubility Parameter Values (δ) and Dispersion Solubility Parameter Values (δ_d) for Isooctane- Chloroform Mixtures

Isooctane:$CHCl_3$ Ratio	δ	δ
100:0	7.0	7.0
85:15	7.3	7.2
75:25	7.5	7.4
50:50	8:1	7.8
25:75	8.6	8.2
0:100	9.2	8.6

Table 11

Overall Solubility Parameter Values (δ) and Dispersion Solubility Parameter Values (δ_d) for Isooctane-Ethanol Mixtures

Isooctane:Ethanol Ratio	δ	δ
100:0	7.0	7.0
91:0	7.5	7.1
82:18	8.1	7.1
72:28	8.6	7.2
63:37	9.2	7.3
0:100	12.7	7.8

As the value of δ_d of the mobile phase approaches that of the beads (assumed to be 9.1), their interaction should increase. As a result, the interaction between the beads and any solute injected onto the column will decrease, reducing retention volumes.

Table 12

Chloroform-Acetonitrile Mobile Phases

$CHCl_3$:CH_3CN Ratio	Solubility Parameter
82:18	9.7
52:48	10.5
0:100	11.9

Table 13

Acetonitrile-Water Mobile Phases

CH_3CN:H_2O Ratio	Solubility Parameter
90:10	13.0
85:15	13.6

Figures 9 and 10 are plots of log k' vs. mobile phase solubility parameter for the mobile phases used in the tables. The elution order for these solutes is again identical to that found for the normal phase made, viz,, benzene, naphthalene, phenanthrene, and pyrene. If the separation mechanism were a true reverse phase mechanism, the elution order should be the reverse of what was observed. This supports the conclusion that the interactions involved in the separation are non-specific, and that the elution order is a function of the size of the molecule.

Mori (11), using a similar polystyrene support, found that the polycyclic aromatic hydrocarbons had the same elution order in both normal and reverse phase modes. If the primary factor affecting the retention behavior of the four solutes is dispersion interactions, it would be interesting to look at the dispersion component of the various mobile phases used. Tables 12 and 13 list both the overall solubility parameters and the dispersion solubility parameters for these mobile phases.

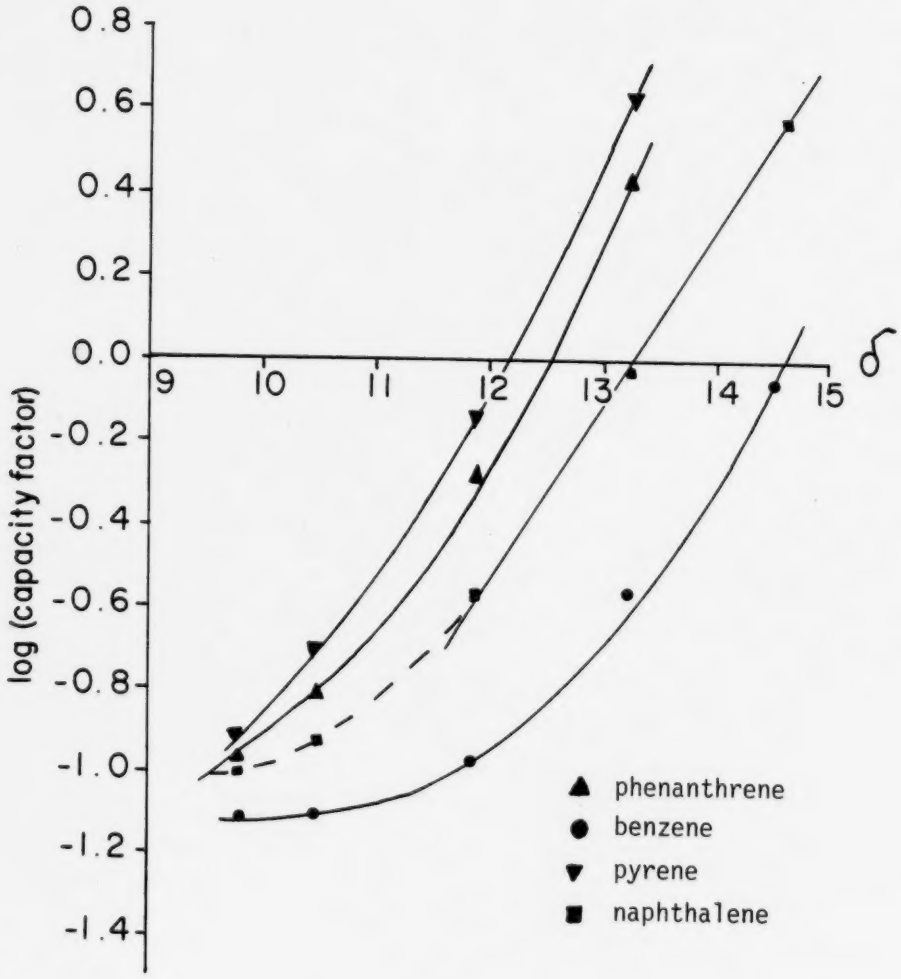

Figure 9. Log (Capacity Factor)-Solubility Parameter Relationship Using Chloroform-Methanol

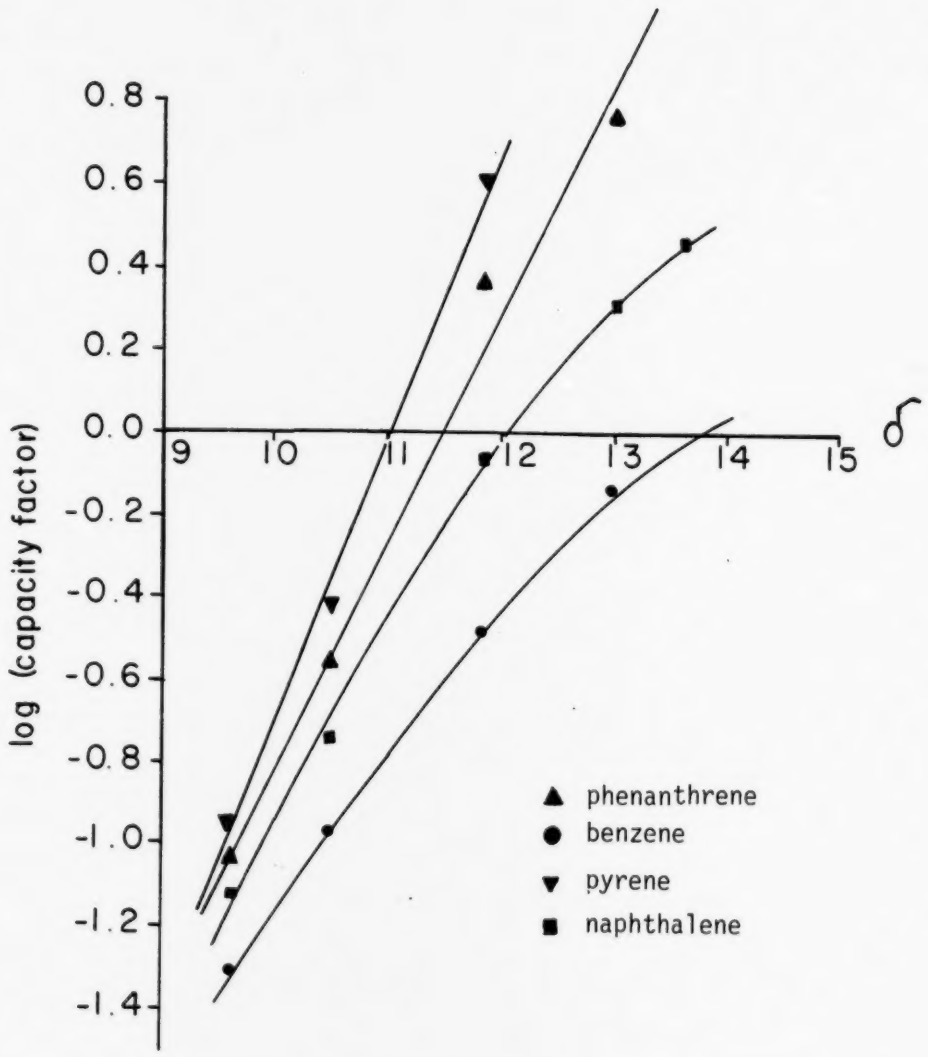

Figure 10. Log (Capacity Factor)-Solubility Parameter Relationship Using Chloroform-Acetonitrile

Table 12

Overall Solubility Parameter Values (S) and Dispersion Solubility Parameter Values (S_d) (12) for Chloroform-Methanol Mixtures

Chloroform:Methanol Ratio	S	S_d
100:0	9.2	8.6
90:10	9.7	8.5
75:25	10.5	8.3
50:50	11.8	8.0
25:75	13.2	7.7

Table 13

Overall Solubility Parameter Values (S) and Dispersion Solubility Parameter Values (S_d) for Chloroform-Acetonitrile and Acetonitrile-Water Mixtures

Chloroform:Acetronitrile Ratio	S	S_d
100:0	9.2	8.6
82:18	9.7	8.4
52:48	10.5	8.1
0:100	11.9	7.5
Acetonitrile:H_2O Ratio		
90:10	13	6.5
85:15	13.6	6.5

Figures 11 and 12 are plots of log k' vs the mobile phase dispersion solubility parameter. Figures 11 and 12 are remarkably similar to Figure 1. The slopes of the lines increase when going from benzene to pyrene, with phenathrene and pyrene showing nearly identical chromatographic behavior. This is identical to Figure 1, in which the solutes were run using a "normal phase" mobile phase. Tables 14 lists the linear least squares

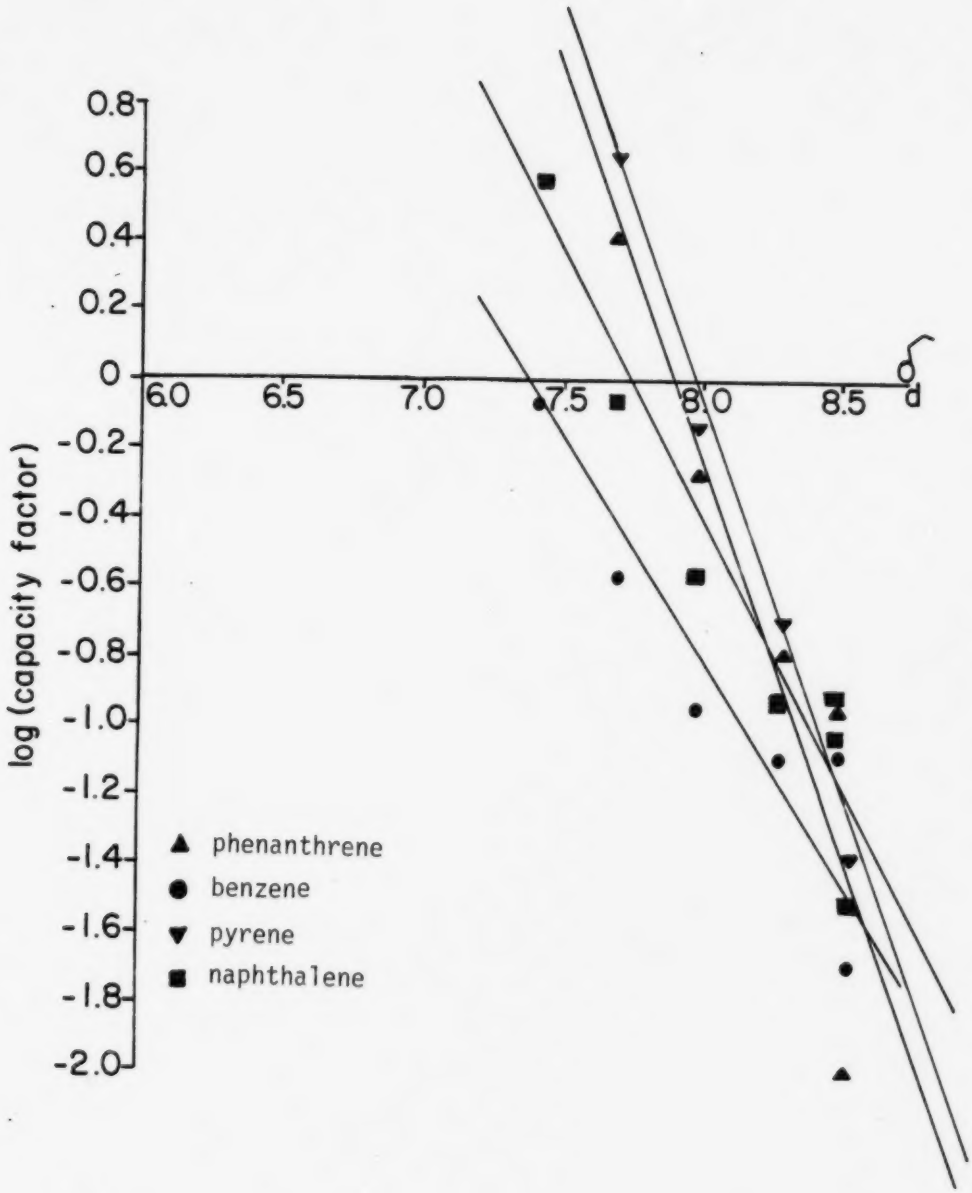

Figure 11. Log (Capacity Factor)-Dispersion Solubility Parameter Relationship for Chloroform-Methanol Mobile Phases

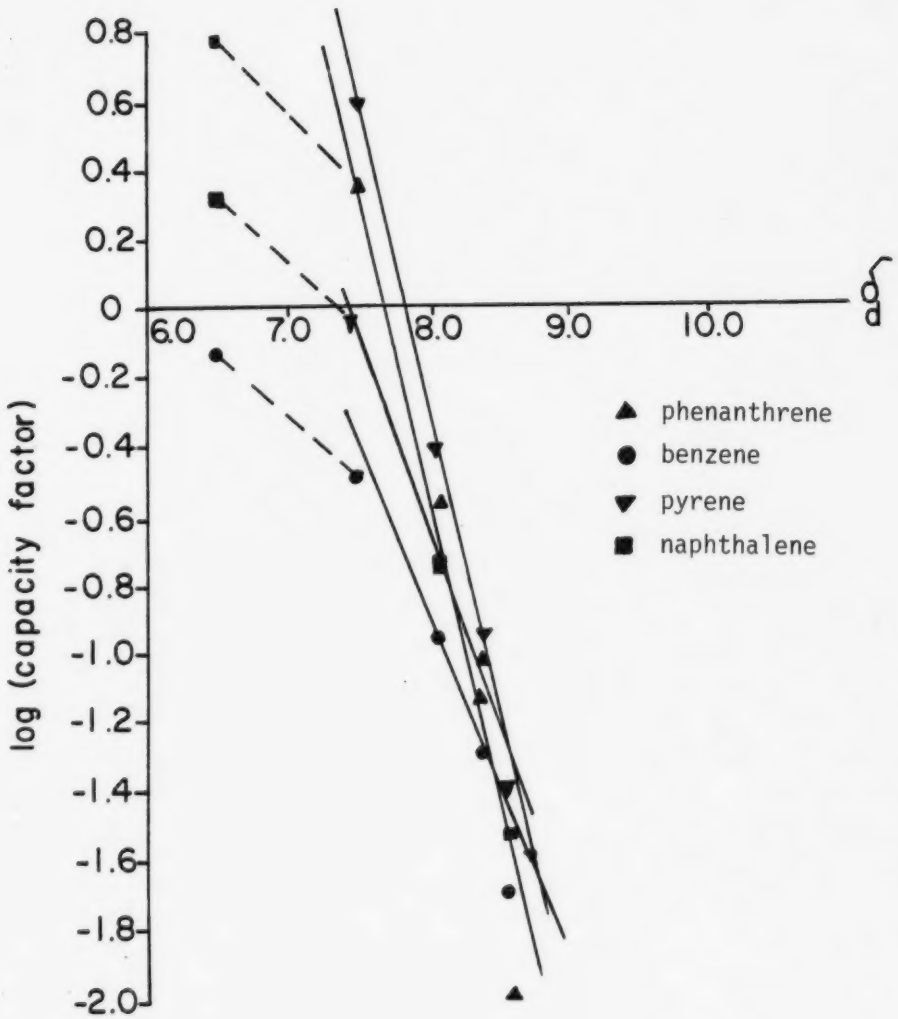

Figure 12. Log (Capacity Factor)-Dispersion Solubility Parameter Relationship for Chloroform-Acetonitrile and Acetonitrile-Water Mobile Phases

correlation coefficient for each of the lines in Figures 11 and 12.

Table 14

Log k' vs. Dispersion Solubility Parameter Correlation Coefficients for Chloroform-Methanol and Chloroform-Acetonitrile Mobile Phases

Mobile Phase	Correlation Coefficient			
	Benzene	Naphthalene	Phenanthrene	Pyrene
$CHCl_3$:MeOH	0.98	0.98	0.94	0.99
$CHCL_3$:CH_3CN	0.98	0.99	0.96	0.99

As Table 14 shows, all of the solutes show very good correlation with the disperion solubility parameter. The addition of water to the mobile phase causes a break in the curves (S_d = 6.5 in Figure 12). This means that the retention volume of the solutes increased to a smaller extent than would be expected. Water in the mobile phase probably deactivates the surface, although its exact effect would be difficult to predict. Nevertheless, although the overall mobile phase would be considered to be reverse phase, it is apparent that dispersion interactions determine the relative elution order and retention volumes of the solutes. Thus, for the polycyclic aromatic hydrocarbons, the larger the molecule the greater its retention volume, regardless of the particular mobile being used.

The relationship between the retention volume and molecular size is further illustrated in Figure 13 and Table 15. Figure 13 is a plot of log k' vs. the number of carbon atoms in the four PAH compounds studied, using acetonitrile as the mobile phase. Table 15 summarizes the data and gives the correlation coefficient for the line in Figure 13.

Table 15

log k' for Benzene, Naphthalene, Phenanthrene, and Pyrene with Acetonitrile Mobile Phase

log k'				
Benzene	Naphthalene	Phenanthrene	Pyrene	Correlation Coefficient
-0.49	-0.05	0.36	0.60	0.999

As the data show, there is a linear relationship between log k' and the number of carbon atoms. When pure ethanol, methanol, and acetonitrile were used as mobile phases, phenanthrene and pyrene did not elute from the column. Presumably, however, a similar linear relationship would also exist when these mobile phases were used instead of acetonitrile. The nature of this relationship may be described by

$$\log k' = a + b N_c \qquad \text{(II-2)}$$

where N_c represents the number of carbon atoms in the molecule, and where a and b are experimentally determined constants. The term a is a function of the stationary phase, while b is a function of both the mobile phase and the solute. It represents the ability of the solute to compete with the mobile phase for sites on the stationary phase; the smaller the value of b, the less tightly bound is the solute. For acetonitrile, the values of a and b are - 1.14 and 0.108, respectively.

When pure chloroform was used as the mobile phase, all of the solutes studied had very small retention volumes, indicating that chloroform has a very high affinity for the stationary phase. Curve 1 in Figure 14 is a plot of log k' vs. the number of

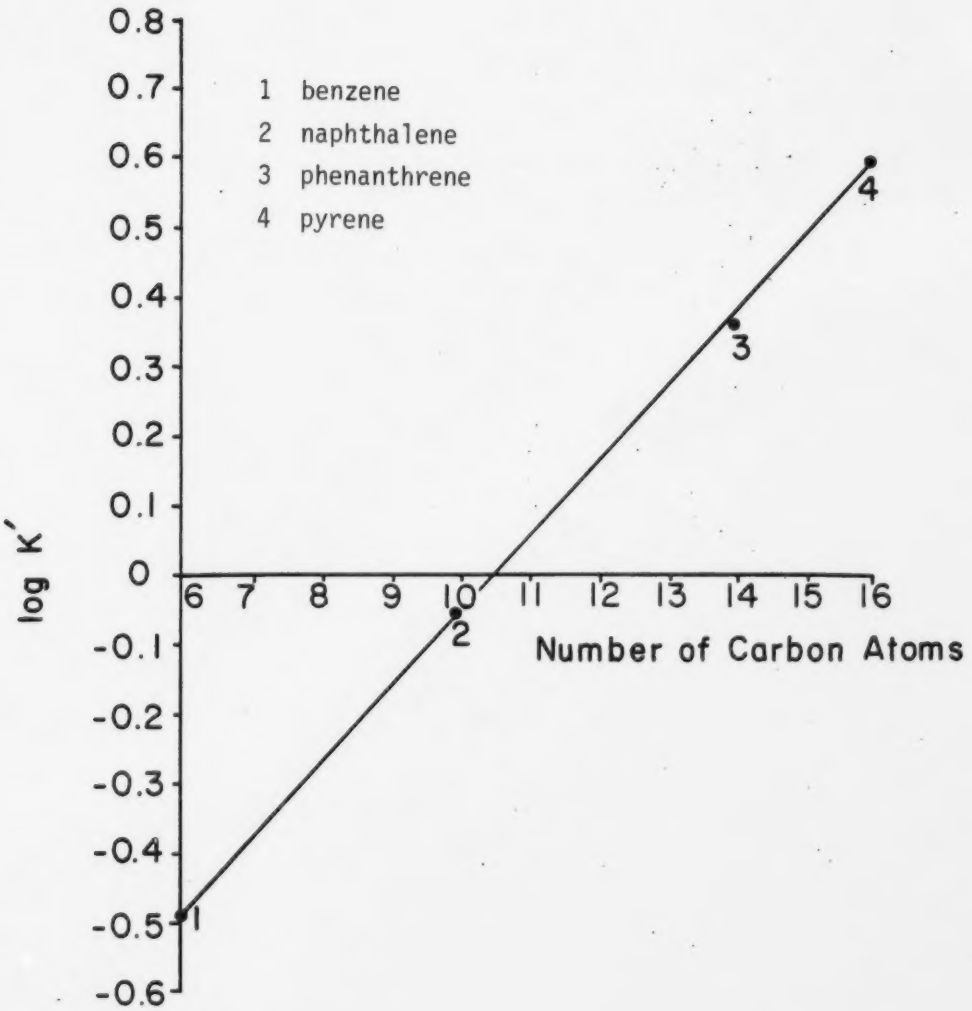

Figure 13. Log k' vs number of Carbon Atoms for Acetonitrile Mobil Phase

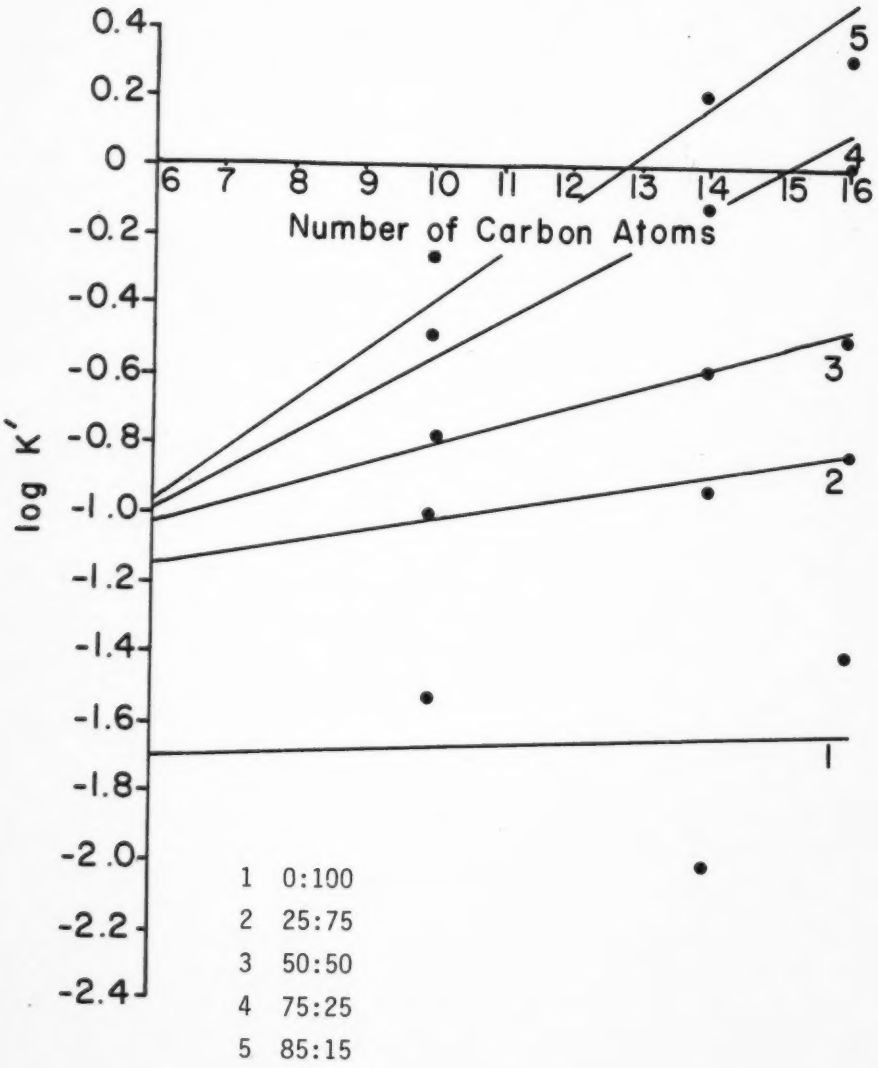

Figure 14. Log k' vs Number of Carbon Atoms for Polyaromatic Hydrocarbons Using Isooctane-Chloroform Mobile Phases

carbon atoms when using chloroform as the mobile phase. As curve 1 shows, ther is very little correlation between log k' and number of carbon atoms when chloroform is used as the mobile phase. The slope of the curve is nearly zero, indicating that chloroform itself has a very strong affinity for the station phase. Curves 2-5 show the data obtained as the percent chloroform in the mobile phase is decreased from 75% to 15%. Table 16 summarizes the data shown in Figure 14. The values for a and b were obtained from linear least-squares regression analysis.

Table 16

Values for a and b in Equation (2) for Isooctane-Chloroform Mobile Phases

Isooctane:$CHCl_3$ Ratio	a	b	Correlation Coefficient
85:15	-1.667	0.130	0.987
75:25	-1.562	0.102	0.992
50:50	-1.354	0.0553	0.996
25:75	-1.330	0.0311	0.990
0:100	-1.719	0.00559	0.095

Similar results were obtained when using chloroform-methanol mobile phases. Figure 15 is a plot of log k' vs. number of carbon atoms for the PAH compounds when using chloroform-methanol mobile phases. Once again, as the percentage of chloroform in the mobile phase is decreased, the slope of the curve increases, indicating that the solute has a greater and greater affinity for the stationary phase. Table 17 summarizes the data shown in Figure 9.

Table 17

Values for a and b in Equation (2) for Chloroform-Methanol Mobile Phases

Chloroform:MeOH Ratio	a	b	Correlation Coefficient
90:10	-1.214	0.0181	0.998
75:25	-1.324	0.0386	0.996
50:50	-1.424	0.0814	0.997
25:75	-1.279	0.120	0.999

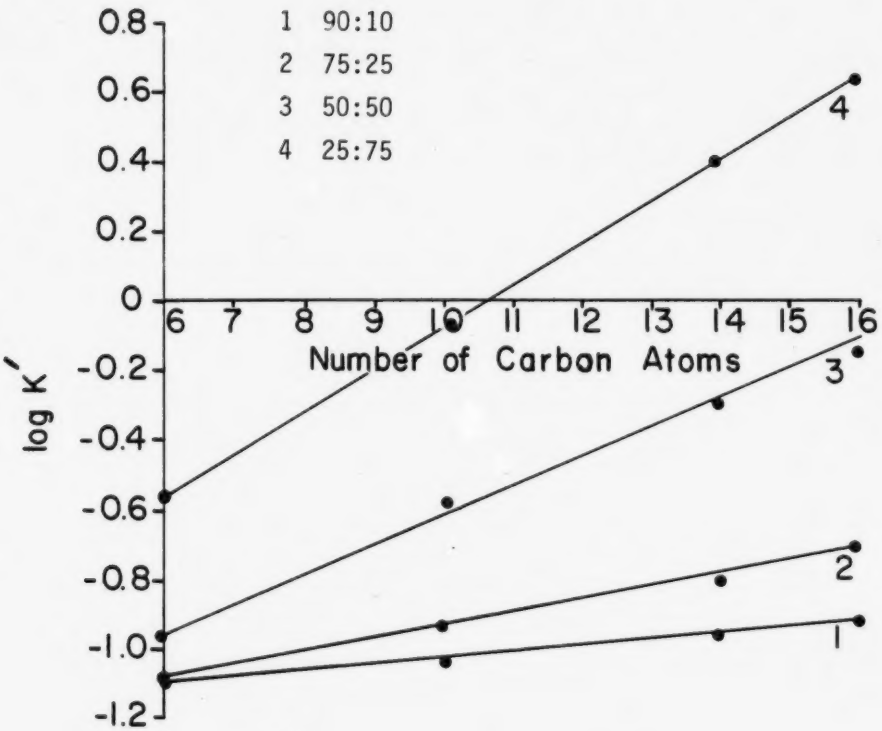

Figure 15. Log k' vs. Number of Carbon Atoms for Polyaromatic Hydrocarbons Using Chloroform-Methanol Mobil Phases

The values of a for both sets of mobile phases remained relatively constant. This indicates that the term a represents some property of the stationary phase that is reasonably independent of the mobile phase used. The actual distribution of a solute between the mobile and stationary phases is not independent of the mobile phase used. The curves in Figures 14 and 15 that correspond to the same percentage chloroform in the mobile phase are not quite superimposable. This indicates that the second component in the mobile phase plays a part in the distribution process, since k' is not dependent solely upon the percentage chloroform in the mobile phase. This is further shown in Figure 16. Figure 16 is a plot of the slope (i.e., term b in Tables 16 and 17) of each curve in Figures 14 and 15 vs. the percentage chloroform in the mobile phase. If the distribution of a solute depended only upon the percentage chloroform in the mobile phase, the two curves in Figure 16 should be superimposed. Although the two curves are very similar, the difference between them is due to the fact that isooctane and methanol do not interact to the same extent with the stationary phase. Thus, the distribution of a solute depends not only upon the amount of chloroform in the mobile phase, but also upon the nature of the second component in the mobile phase.

These results indicate that the distribution processes involved in the D-814 beads cannot simply be described as purely liquid-liquid or liquid-solid chromatography. When pure solvents such as isooctane, ethanol, methanol, or acetonitrile, which do not have strong affinities for the beads, are used as mobile phases, the beads act more as a solid. The chromatographic behavior of solutes using these mobile phases may be further described in terms of liquid-solid chromatography. When chloroform is used as the mobile phase, the chloroform has such a strong affinity for the beads that it essentially excludes other solutes from interacting with the beads. When solvent mixtures containing chloroform are used as mobile phases, the effect of the chloroform is related to its proportion in the mobile phase. The presence of chloroform results in a separation mechanism that is some type of combination of both liquid-liquid and liquid-solid chromatography.

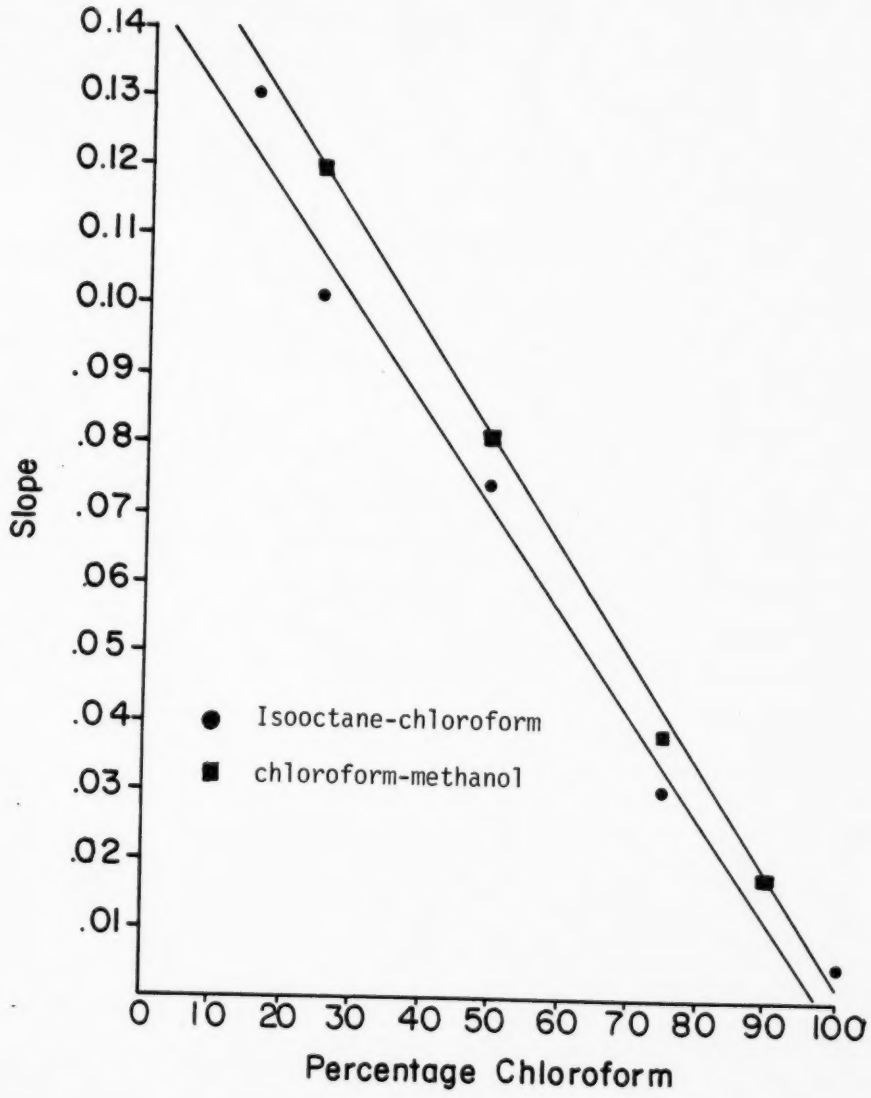

Figure 16. Slope of Log k' Curves vs Percentage Chloroform in Mobile Phase for Polyaromatic Hydrocarbons

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III. TECHNIQUES FOR THE MEASUREMENT OF CARBON IN ATMOSPHERIC PARTICULATE MATTER

INTRODUCTION

The carbon fraction of atmospheric particulates, which can account for 10-90% of the total mass, is currently not well characterized in air quality studies. Several investigators (e.g., see Appel et al., 1979) have studied individual hydrocarbons and certain classes of organic compounds in various atmospheric particulate samples. Such studies, however, can determine only a fraction of the total carbon composition. Historically, extraction and gravimetric techniques have been used to determine "organics" on high volume samples. These techniques suffer, however, from both a lack of sensitivity and questions about what is actually being measured.

This research effort was aimed at providing reliable, sensitive methods for measuring atmospheric particulate carbon (and the type of carbon) which can be effectively and efficiently used with the types of samples commonly collected in air quality monitoring and evaluation efforts. Efforts included a determination of optimum conditions for measuring total particulate carbon by high temperature combustion and evaluating the potential problems and reliability of this measurement technique. These studies demonstrated that high volume samples collected on quartz and glass fiber filters can be analyzed in a very sensitive and reproducible manner using a commercial CHN analyzer if the analysis and sample handling conditions and equipment are modified to accommodate these types of samples. Additional studies were carried out on procedures for the classification of carbon types.

EXPERIMENTAL

A. Combustion Techniques

For this work, a Perkin-Elmer Model 240 Elemental Analyzer was used. Initial work with particulate samples suggested it was necessary to construct two special pieces of equipment for measuring carbon collected on filters. The first was a filter cutter made from a block of tool steel with a 5.4 mm x 49.5 mm rectangular recess machined into the bottom and the perimeter of this recess ground to an edge. In use, the filter was placed on a sheet of soft aluminum and the cutter placed on the filter and tapped with a hammer. The resulting piece of filter was equal to 2.67 cm^2 (0.657%) of a standard 9" x 7" filter. This provided a sample with maximum surface area to fit into the modified ladle.

The modified ladle was a quartz ladle attached to an open cylindrical tube of 6-mil platinum foil measuring 51 mm in length x 8.5 mm in diameter. If glass filters were run, a second piece of platinum foil was rolled up, forming a tube which fit snugly into the first Pt tube. A section of filter was punched out with the filter cutter and carefully inserted into the inner cylinder. The ladle and sample were then handled as a normal sample. When the run was over, the inner cylinder was carefully removed, unrolled, and flexed until the glass bead came free. With very clean samples, scraping was sometimes necessary. This was done most conveniently with fingers, as the tube, after being re-rolled, could be easily and effectively cleaned by flaming over a burner.

There were several advantages in using this type of ladle. One was that large surfaces of platinum were exposed and the catalytic action produced was found desirable to ensure complete combustion. Another advantage was that an

adequately large sample could be introduced without folding. This was desirable, as it produced as much oxidation and volatilization as possible before particles were entrapped by the softening glass. A third advantage was that the resulting glass bead could usually be removed fairly easily.

Since glass fiber filters were used for the collection of particulate matter and since these soften and flow at the temperatures encountered in the elemental analyzer, thus trapping some material before it can be oxidized, it was necessary to investigate the recovery of both elemental and organic carbon from sections of glass filter. Accordingly, experiments were designed to impregnate sections of filter with charcoal, graphite, and with organic substances (and to measure the carbon recovered).

All experiments indicated that the measurement of total carbon on glass fiber filters could be carried out using standard operational procedures for the CHN analyzer. There was no evidence of incomplete combustion or the "trapping" of carbon in the melted glass. While glass fiber filters may have sampling drawbacks (artifact formation) it is possible to quantitatively measure the carbon collected from the atmosphere. Quartz filters were preferred for this analysis since sampling artifacts were reportedly minimized. Additionally, there was no problem with the substrate melting under normal measurement conditions.

B. Solvent Extraction of Atmospheric Particulates

Some efforts were devoted to the development of a suitable series of selective extraction solvents that would provide an effective preliminary fractionation of the organic constituents of airborne particulate matter. An evaluation of optimum extraction parameters and procedures was made. For this work a micro-extraction system was designed for use under hot (reflux) or cold (ultrasonics) extraction conditions. Figure 17 presents a diagram of this system. Extractions were carried out by placing a section of filter in the flask with 0.1-1.0 ml of solvent. The sample was then extracted with refluxing or using ultrasonic agitation. The filter and dislodged particles were centrifuged to the bottom of the flask and solvent evaporated to 0.5 ml. Eighty percent of this solvent was then added to a platinum boat and evaporated to dryness. The residue was combusted in an automated (CHN) analyzer and the carbon content determined. For a 24-hour dichotomous filter sample in which one-fourth of the filter was extracted, this provided a sample equivalent to 4.8 m^3 of air. Total carbon analysis on the quartz filter indicated that for these samples there were 10 to 100 µg of total C to work with.

When working with this small amount of organic material, it was obviously necessary to exercise every possible care in handling and manipulating samples and solvents to avoid blank problems. For this work, high purity and/or redistilled solvents were used. Several workers have demonstrated the advantages of using mixed polar and non-polar solvents (Grossjean, 1975; Gordon, 1974; Appel, et al., 1976, 1979).

A majority of the work performed on the extraction of Teflon filters was centered around a way to control the blank problems associated with this type of analysis. By careful choice of pure solvents (isopropanol - toluene) and handling methods, it was possible to reduce extractable carbon blanks to the

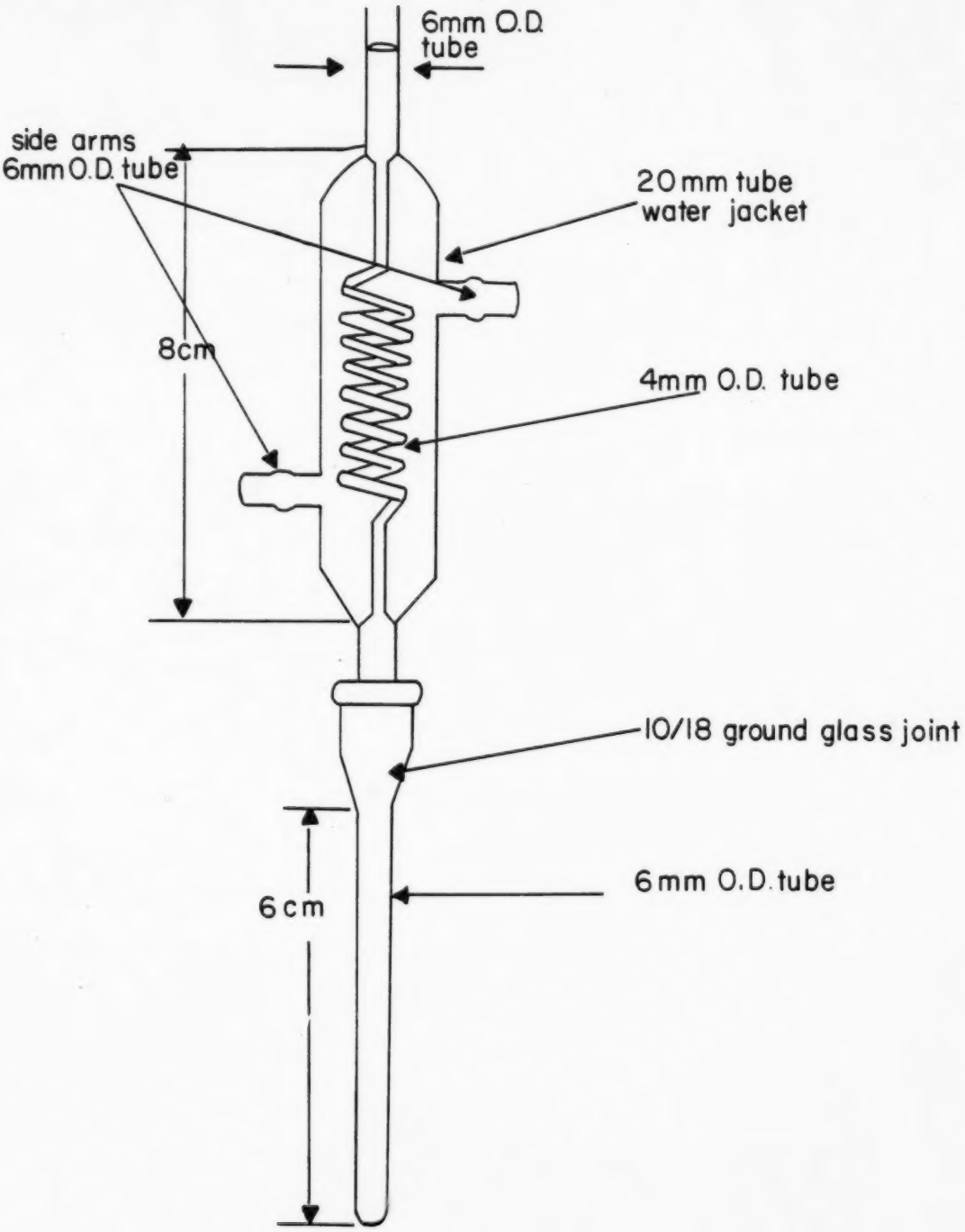

Figure 17. Microextraction System

values shown in Table 18. The polyethylene ringed Teflon filters (GHIA Corporation, Pleasanton, Calif.) were found to have reasonably low blank values. Table 18 presents a comparison of blank results for the Teflon and quartz filter media as received from the manufacturer. Weighing and loading of the filters into the dichotomous samplers (Sierra Model 240) may increase these blank values by an order of magnitude or more. It was necessary to thoroughly clean the sample holder with methanol every time it was used. Additionally, it was found that blanks were reduced and more reproducible if the Model 240 sampling system was thoroughly cleaned with methanol regularly. We suspect the various O-ring seals and silicone lubrication used in the Model 240 (manual Dichotomous Sampler) were primarily responsible for the blank problems encountered. With such precautions it was possible to obtain field blank values (weighed-loaded, etc.) only slightly higher (ca. 50%) than the values presented in Table 18. Thus, we presently conclude that if extreme care in preparing and handling of samples is exercised, dichotomous Teflon filter samples with carbon blanks acceptable for subsequent organic and carbon analysis may be obtained.

As previously mentioned, comparisons were made between reflux-continuous extraction procedures and a batch extraction using ultrasonic agitation of the samples. Table 19 presents example extraction (isopropanol - toluene) results for ultrasonic and refluxing solvent extraction of replicate (4) samples. All tests of this type have shown the ultrasonic extraction efficiencies to equal or exceed that obtained via the refluxing technique. This technique may be performed in a completely closed extraction container and lends itself well to batch operation.

Table 20 presents an example of the analysis precision obtained using the extraction-carbon analysis procedure described above. Considering the

Table 18

Blank Values and Extraction Efficiencies
for Dichotomous Sampler Filters

Filter		
Quartz	2 $\mu g/cm^2$	(0.3 $\mu g/cm^2$ if heated to 500°C)
Teflon	4 $\mu g/cm^2$	

Table 19

Comparison of Hot and Cold Extraction Techniques

Total C	Quartz Filter Solvent Reflux	Ultrasonic Extraction
129 µg/filter	51 ± 6 µg C/filter	50 ± 5 µg C/filter
	Teflon Filter	
	82 ± 8 µg C/Filter	105 ± 10 µg C/Filter

combination of blank variability and analysis precision, we found that extracted carbon measurements precision for either quartz or Teflon filters was ±5-10 µg C or 6-7% (relative), whichever was larger.

Table 20

Carbon Analysis Precision of Replicate Samples:
Extracted and Remaining Carbon
(Quartz Filters)

Section	Extracted Carbon (µg/filter)	Remaining on filter	Ext Efs
1	33.5	71 µg	33%
2	43.1	73 µg	37%
3	37.8	68 µg	36%
4	45.8	77 µg	37%
Avg	40.1 ± 6 µg/c	72 ± 4 µg/c	

It is important to note that the extraction procedures being used in our laboratory with quartz dichotomous filter samples consistently show extraction efficiencies between 30 and 60% of the total carbon (as determined by direct combustion of the filter). Similar results were reported for high volume aerosols in California (Appel, et al., 1979; Navaho, et al., 1978). The fact that approximately 50% of the carbon content of atmospheric aerosols is apparently not extractable in organic solvents implies the need to obtain a better understanding of what this material might be. Experiments are still in progress to determine the extractable carbon and extraction efficiencies of samples collected simultaneously on quartz and Teflon filters. Initial results suggest that a large amount of non-extractable carbon is also present

on the Teflon filters (i.e., the low extraction efficiencies is not an artifact of the quartz sampling media).

Our efforts aimed at measuring organic aerosol carbon centered primarily on the development and evaluation of extraction procedures suitable for use with dichotomous filter samples. However, a limited amount of work was performed on using acidification and wet oxidation techniques to measure inorganic carbon and organic carbon on collected aerosol samples.

C. Carbonate-Bicarbonate Measurement

The inorganic carbon ($CO_3^=$, HCO_3^-) content of particulate matter was determined by acidification of the sample and measurement of evolved CO_2. A portion of sample was added to an ampul which was then purged with He. A valving system was developed which allowed introduction of acid to the sample without any air contamination. The evolved CO_2 was collected and analyzed as subsequently described. This method is straightforward and appears to be suitable for use with filter samples of particulate matter. Replicate analysis showed the precision of the measurement to be better than ±10%. For the samples evaluated, the inorganic carbon was less than 10% of the total C (as measured by the combustion procedure). Table 21 presents a summary of results obtained for inorganic carbon content of high volume samples collected on quartz filters.

Table 21

Inorganic Carbon Contents of Bulk and Size Separate Particulate Samples in Urban and Rural Southern Arizona

Urban	% of Total Carbon	$\mu g/m^3$
Small Particles (n = 12)	1-7% (average of 3%)	0.02 - 1 $\mu g/m^3$
Bulk Samples (n = 10)	8-15% (average of 11%)	0.3 - 4 $\mu g/m^3$
Rural (n = 18)	<1-4% (average of <2%)	<0.02 - 0.1 $\mu g/m^3$

D. Light Absorption

During this project a combination of heat treatment (followed by carbon and C/H analysis) and light absorption measurements were evaluated to determine if either or both would be suitable for measuring elemental carbon. One method of elemental carbon determination involved heating the sample to 500°C to remove the organics, followed by a combustion measurement of the remaining carbon. Rosen et al. (1977) presented circumstantial evidence that this type of sample treatment and measurement is a good approximation of elemental carbon. Our results from studies to date are consistent with this suggestion. Some questions still exist, however, about this method of determining the primary carbon. First, it has not been demonstrated that the heat treatment will remove all organic carbon compounds found in atmospheric particulate matter. Secondly, there is some evidence that elemental or soot-like carbon is actually produced by pyrolysis and charring with the heat treatment used (at least when rapid sample heating occurs in an inert atmosphere).

Another method investigated for soot determination involved the measurement of the absorption coefficient of the aerosol combined with combustion measurements of carbon and the C/H ratio. Rosen et al. (1977) suggested that the aerosol absorption of light is almost totally dominated by the soot-like carbon present. If this is true, and if the absorption coefficient of the soot is constant and can be defined, then a simple aerosol absorption measurement would be a direct indicator of the elemental carbon. Thus, a combination of the absorption measurements using essentially the method of Lin et al. (1973) and combustion measurements were used on various standards and samples to determine the degree to which "charring" occurs and the "constancy" of the apparent soot absorption coefficients. Our work showed that: 1) Charring of a sample as measured by the increased absorption of light by the sample does

occur (this charring, however, can apparently be held to a few percent of the soot present on both rural and urban high volume samples if heating is done slowly); and 2) For a series of samples collected in Tucson and a rural area 70 miles southeast of Tucson, the apparent carbon absorption coefficient is approximately the same at each location.

Figure 18 presents apparent absorption (and carbon concentration) versus heat treatment temperature. In this figure, it is seen that with heat treatments of 400°-500°C the optical density of the sample increases while the total carbon concentration decreases. These experiments were carried out by conducting the heating under nitrogen. The sample was inserted into a tube furnace equilibrated at the indicated temperature for a period of one hour. Two points should be noted about these results. The first is that this method of treatment results in a pyrolysis or "charring" which actually produces the type of carbon being measured. Secondly, the decrease in absorptivity at temperatures above 500°C results from oxidation of the carbon by oxygen contamination when the sample is introduced into the furnace. Subsequent experiments with care taken to eliminate any oxygen from the system showed that the absorptive material is stable. It was also shown that the degree of charring (as measured by the increased light absorption) could be held to smaller values if heating was performed slowly (e.g., 25°C to 500°C in two hours).

While the above-described light absorption measurements will be of importance to the heat treatment-carbon measurement method of characterizing carbonaceous materials, it is felt that it will be of great importance for the direct estimation of soot and possibly as an indicator of total organic carbon.

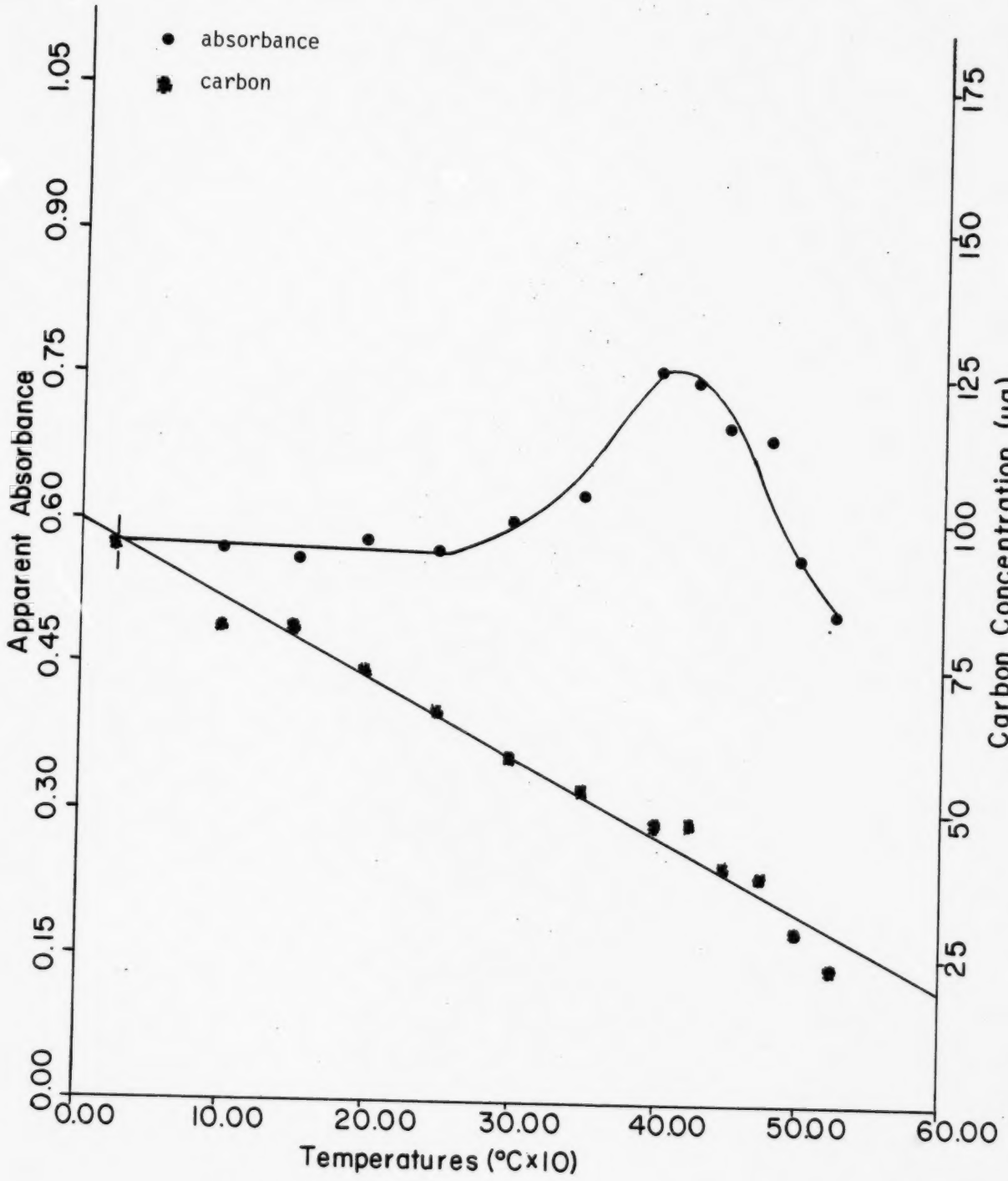

Figure 18. Changes in Carbon Content and Apparent Absorbance as Function of Heating

In light absorbing media, the extinction coefficient is related to the refractive index in the following form:

$$N = n - i\,k \qquad \text{(III-1)}$$

where n is the real refractive index and N the complex form. The extinction coefficient (or imaginary part of the refractive index), K, is defined by

$$k = \lambda \ln (I_o/I_a)/4\mu t \qquad \text{(III-2)}$$

when absorption reduces the intensity of light from I_o to I_a in transversing a thickness t.

Figure 19 presents apparent absorption (at 6250 $\mathring{A}$) versus carbon concentration for 32 high volume samples (glass fibers) collected at Tucson and a rural location approximately 65 miles southeast of Tucson. (See Moyers et al., 1977) The atmospheric carbon concentrations for these samples range from 1 to 30 $\mu g/m^3$. The one outlying sample is to be reanalyzed. From the slope of this line, it may be shown that the apparent total carbon extinction coefficient (k) is approximately 0.1. These samples are currently undergoing the heat treatment and reanalysis (both absorption and carbon). Although this work is still in progress, the few samples already analyzed showed apparent elemental carbon concentrations at 25-35% of the total carbon values indicated in Figure 19. Thus, the extinction coefficient for the "soot" would be approximately 0.3 to 0.4. This value is in good agreement with the optical extinction coefficient of soot as determined by Dalzell and Sarofim (1969) and Chippet and Gray (1978).

The measurement of the light absorption of aerosols by the above discussed techniques offers several attractive potentials and advantages for use as monitoring techniques in air pollution research and control efforts.

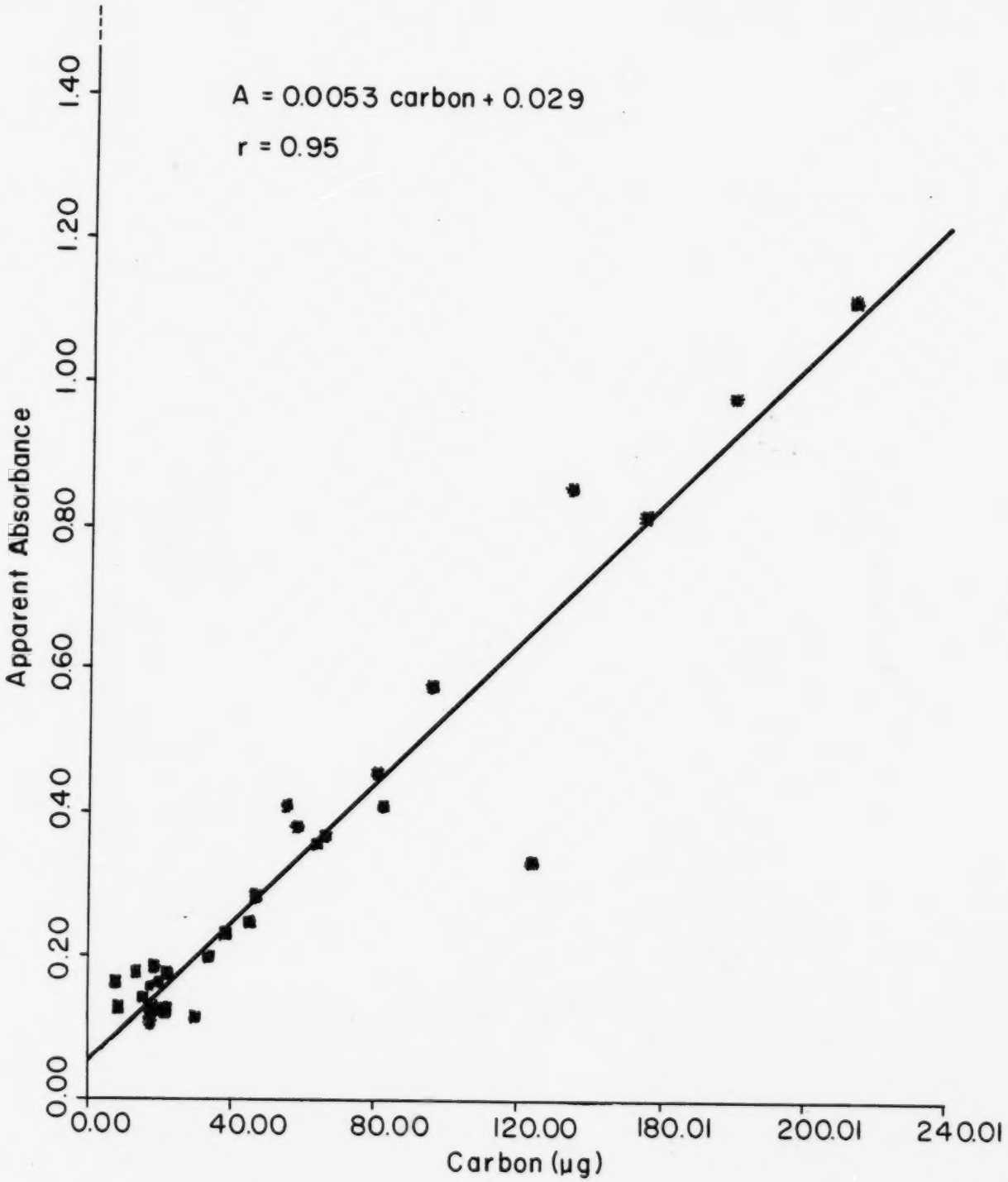

Figure 19. Apparent Absorbance vs Carbon Concentration for Aerosol Samples from rural and Urban Atmospheres of the Southwest

First, the technique is very inexpensive and simple to use. Almost any laboratory spectrophotometer could be used to make these measurements. The sample holder and appropriate lenses should cost no more than $50 for construction and installation. Alternatively, a very simple device consisting of a light source, an interference filter, appropriate optics and geometry, and a simple detector could easily be constructed to read high volume (or other types of filters) aerosol samples without any type of sample preparation whatsoever (slide between source and detector and measure apparent absorbance). Another advantage is the speed and ease of measurement (simpler than weighing). Such measurements potentially provide information about $b_{abs\text{-}aerosol}$, soot content, and perhaps a good estimate of total organic content and TSP (assuming the soot-to-carbon and soot-to-TSP ratios are approximately constant at a given location).

E. Wet Oxidation of Teflon Filters

During the past five years, aerosol collection of low volume filters using Teflon membrane as a collection matrix has become increasingly popular in various air pollution research programs. Teflon filters are essentially chemically and physically inert and are well suited for use with the multi-element analysis technique of x-ray fluorescence. Obviously, the determination of carbon containing species on Teflon filters is complicated by the carbon matrix and the small amount of collected sample (typically 0.5 - 1.0 mg).

In this project, determinations of particulate carbon using peroxy-disulfate oxidation of urban aerosol samples are discussed. The purpose of this study was to determine the total organic carbon contents of atmospheric aerosols by the method routinely used in oceanographic studies of organic carbon. Additionally, the organic carbon determination was focused at aerosol samples collected on Teflon membrane filters because carbon determination, using methods presently employed, is not possible due to the interference by the carbon matrix of the Teflon filter. A slight modification of peroxydisulfate oxidation from that mentioned in the literature is made in this report in order to apply this method to samples collected on Teflon material. It should be pointed out that although this method is widely used for the analysis of dissolved organic carbon, the oxidation efficiency of peroxydisulfate is controversial. Some workers reported the efficiency ranging between 50% to 90% or greater in comparison with other techniques. The study by Menzel and Vaccaro (1964) indicated that 100% recovery was found for a series of organic compounds dissolved in seawater. Since carbonaceous species present in the particulate matter are both sooty and organic (inorganic is, in most cases, negligible), this wet oxidation method is not necessarily a measure of the total organic carbon. Therefore,

this method has been defined, operationally, as a method for 'oxidizable or reactive' carbon.

An Oceanography International Corp. (Model PIR-2000) nondispersive IR analyzer was employed for CO_2 measurement. Nitrogen was used as a carrier gas at a flow rate of 200 ml/min. Special sampling systems were designed to collect total suspended particulates simultaneously on a Teflon membrane filter and a quartz fiber filter. Those filters were all in circular shapes with the approximate diameters of 37 mm and were sampled for 12 to 48 hours at a flow rate of 1 lpm approximately.

For oxidation of the samples, $K_2S_2O_8$, 10% H_3PO_4, 0.5 M NH_4Cl and distilled, deionized water were used. For TFE filters 10^{-3} M NH_4Cl was added to the sample to increase the "wetability" of the TFE. The oxidation efficiency of the various organic compounds were tested by using this measurement technique. Data from these tests are presented in Table 22.

In past work, sugar and acid compounds were shown to be completely oxidized (Menzel and Vaccaro, 1964). Again, those compounds were successfully analyzed in this project. However, a series of oxidation studies (see Table 22) showed that some organic compounds could not be completely oxidized. Polystyrene and polyaromatic-ether-ketone-sulfone are polymeric substances which could not be oxidized at all. In addition, the CO_2 recovered from graphite was negligible. Also, the oxidizable carbon content of NBS urban particulates were measured and ranged from 60% to 70% of the total carbon (compared to combustion methods).

Both quartz and Teflon blank filters were analyzed for their carbon content by peroxydisulfate oxidation, and a Perkin-Elmer 240 Elemental Analyzer. Results of the blank filters are shown in Table 23. Carbon concentrations of blank quartz filters via the oxidation method is observed to be higher than

Table 22

Recovery of Organic Carbon From a Variety of Organic Compounds and Sources

Sample	% Recovery
Benzoic Acid	101.4 ± 0.2
Malic Acid	99.4 ± 0.3
Oxalic Acid	97.9 ± 8.2
Carminic Acid	100.7 ± 5.9
Brucine	100.6 ± 4.2
Sucrose	104.4 ± 2.2
Graphite	< 2
Polystyrene	< 2
Polyaromatic Ether-Ketone Sulfone	< 2
NBS Urban Particulate #1648	73.1 ± 3.5

Table 23

Blank Filters Analysis of Carbon

PEROXYDISULFATE OXIDATION		COMBUSTION
Teflon ($\mu g/cm^2$)	Quartz ($\mu g/cm^2$)	Quartz ($\mu g/cm^2$)
5.68	7.69	6.34
2.94	8.26	7.52
7.13	9.01	8.22
5.00	11.04	5.14
5.19 ± 1.74	9.0 ± 1.46	6.81 ± 1.35

those obtained by a CHN analyzer. These differences in carbon concentrations between the two methods can be attributed to the error that might be involved in the sample preparation processes. There are many more steps involved in the wet oxidation than required for the combustion procedure.

The determination of carbon by combustion and wet oxidation for a series of samples collected on quartz fiber filters is shown in Table 24. The carbon concentration measured by wet oxidation ranged from 60% to 100% of each corresponding total carbon which was measured by employing a CHN analyzer. Some sample discoloration occurs in the wet oxidation procedure, indicating that the elemental carbon present in the particulate samples is perhaps oxidized to some extent.

Table 24

Carbon Determination in Atmospheric Particulates

Sample	Combustion (C $\mu g/cm^2$)	Wet Oxidation (C $\mu g/cm^2$)	Ratio $\left(\frac{\text{Oxidation}}{\text{Combustion}}\right)$
538A	44.7	29.6	0.66
539A	29.7	25.3	0.85
540A	22.9	22.2	0.97
541A	23.9	19.5	0.82
542A	29.5	29.7	1.01
543A	41.6	31.3	0.75
544A	39.2	36.6	0.93
545A	41.1	37.1	0.90
546A	36.1	33.7	0.93
547A	30.1	25.7	0.85

Due to the floatability of Teflon filters and their hydrophobic behavior in water, wet oxidation is not successful when such filters are treated in the same manner as quartz filter samples. Various approaches were attempted to solve the floatation problem of Teflon filters. One method consisted of attaching a heavier substance such as aluminum foil or nichrome wire to the filter samples. However, the results proved to be unsuccessful as the Teflon filters remained floating. Another method was to insert the Teflon filters as far down into the ampule neck as possible so it would be free from burning when the ampule was sealed. The sealed ampules were then tipped upside-down into a rack, which was fitted in the pressure cooker. Though the filters were trapped in the solution, oxidation was not successful because the particulates were not oxidized. However, Teflon filter samples appeared to be significantly decolorized in 0.5 ml of 0.5 M NH_4Cl. It is suggested that the atmospheric particulates collected on Teflon filters could be more accessible to the oxidizing agent since the use of NH_4Cl allows more efficient wetting of the Teflon surface. Table 25 shows the concentrations of carbon measured by wet oxidation on simultaneous samples collected on quartz and Teflon filters.

In most cases, the oxidizable carbon contents determined from Teflon filter samples are slightly less than the oxidizable carbon obtained from quartz filter samples for a given data. Although two different collection matrices do not yield equal measurements of oxidizable carbon, the ratio of oxidizable carbon collected on Teflon over those of quartz is about 0.81 on the average.

The work accomplished under this project makes the oxidation of carbon on TFE filters by peroxydisulfate appear to be a very promising method for future air pollution research and monitoring programs.

Table 25

Carbon Determination by Oxidation with Peroxydisulfate of Atmospheric Particulates Collected on Quartz and Teflon Filters

Sample	Quartz ($\mu g/1.15\ cm^2$)	Teflon ($\mu g/1.15\ cm^2$)	Ratio $\left(\frac{\text{Teflon}}{\text{Quartz}}\right)$
1	30.23	16.70	0.54
2	24.15	15.54	0.64
3	19.31	12.53	0.65
4	19.72	17.01	0.86
5	21.30	18.08	0.85
6	51.58	16.47	0.76
7	11.47	13.23	1.16
8	20.42	17.45	0.83
9	17.93	13.46	0.75
			Avg. Ratio = 0.81 ± 0.16

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